Recycling, Reuse, and Resource Recovery from Fly Ash

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Abstract

Fly ash (FA) is a particulate residue from power plant boiler by burning oil or biomass. In this study fly ash was used to (a) remove total organic carbon (TOC) from intake water; (b) clean up an offshore oil spill; and (c) compost and stabilize municipal sludge. Firstly, oil fly ash (OFA) from oil-fired power plants was characterized, cleaned, homogenized, and activated to prepare activated carbon (AC). Since the drinking water from many small communities in the province of Newfoundland and Labrador has high levels of dissolved natural organic matter (NOM) in their water intake sources, causing the formation of disinfection by-products (DBPs) which are harmful to health, the AC from OFA was used to reduce DBP formation in the drinking water by removing NOM before chlorination. The NOM is typically measured as TOC. The results showed that the AC from fine and coarse OFA could remove 90% and 60% of the TOC from the source water, respectively. Secondly, acid treated OFA and activated carbon obtained from OFA (AC-OFA) were used to remove oil from the surface of water, by agglomerating oil droplets to form larger particles which could attach with the OFA. Due to the nature of hydrophobic, both OFA samples can keep floating on the water surface without sedimentation. The oil adsorption capacity of OFA could go up to $1.08\frac{g\ oil}{g\ OFA}$. Thirdly, fly ash (FA) from the Corner Brook Pulp and Paper mill (CBPP) was used to compost municipal sludge from the Riverhead Wastewater Treatment Plant (RHWWTP) in St. John's. The study shows that the CBPP FA was very effective in reducing polycyclic aromatic hydrocarbon (PAH) levels in the sludge which reached about 90% reduction. These applications show that FA, a waste residue, can be converted into a valuable resource.

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List of Abbreviations

AC: Activated Carbon

ASTM: American Society for Testing and Materials

ATR: Attenuated Total Reflectance

BDCAA: Bromo Dicloro acetic acid

BDCM: Bromo dicloro methane

BET: Brunauer, Emmett and Teller

CBPP: Corner Brook Paper and Pulp Plant

CFA: Coal Fly Ash

DBAA: Dibromo acetic acid

DBCAA: Dibromo chloro acetic acid

DBCM: Dibromo chloro methane

DBPs: Disinfection By-products

DCAA: Dichloro acetic acid

DOEC: Department of Environment and Conservation

DWSP: Drinking Water Surveillance Program

EC: Electrical Conductivity

ESP: Electrostatic Precipitators

FA: Fly Ash

FTIR: Fourier Transform Infrared Radiation

GI: Germination Index

HAA: Halogenated Acetate Acid

HFO: Heavy Fuel Oil

ICP-MS: Inductively coupled plasma mass spectrometry

KBr: Potassium Bromide

MBAA: Monobromo acetic acid

MCAA: Monochloro acetic acid

Na_2SO_4: Sodium sulfate

NaCl: Sodium chloride

NAP: Naphthalene

NOM: Natural Organic Matter

OFA: Oil Fly Ash

PAH: Polycyclic aromatic hydrocarbon

PHEN: Phenanthrene

PM: Particulate Matter

RHWWTP: Riverhead Wastewater Treatment Plant

SEM: Scanning Electron Microscopy

TBAA: Tribromo acetic acid

TCAA: Trichloro acetic acid

TG: Thermogravimetric

THM: Total Halogenated Methane

TOC: Total Organic Carbon

WA: Wood Ash

XRD: X-ray Diffraction

Chapter 1. Introduction

1.1 Background

Fly ash (FA) is the residual waste generated by the combustion of crude oil, heavy fuel oil, coal and hogged fuel in power plants, water desalination systems, and other industrial applications. FA is collected by particulate collection devices such as cyclones and electrostatic precipitators (ESP). Thousands of tons of FA are generated worldwide daily, most is dumped directly into landfills.

FA contains concentrated heavy metals and other impurities. These metals can leach into soil and groundwater. While FA is being transported, the fine particle portion can potentially be blown away by the wind and cause air pollution, and subsequent health issues. OFA has a relatively low density and is potentially hazardous to the environment and human health. The main source of air pollution is fine particulate matter (PM). Recently, research on the effects of oxidant on heart and lung by the inhalation of residual OFA has been conducted through animal studies (Heck et al., 2014, Marchini et al., 2014). Heck et al. (2014) illustrate that exercising after inhaling PM will vastly increase its concentration in lipid peroxidation in the lungs. Thus, inhaling OFA will increase stress on the heart and lungs. Almost 98% of transition metal particles and 78% of carbon particles in OFA are below 2.5 μm (Heck et al., 2014). Marchini et al. (2014) illustrated that during an animal exposure experiment, serious cardiac oxidation will occur after three hours' acute inhalation of OFA. Marchini et al. (2014) demonstrated that ultra-fine particles and transition metal

PM could reach the circulation within hours. Their findings further proved that air pollution caused by fine PM could strongly relate to tissue oxidation and cardiac diseases (Marchini et al., 2014).

Compared with coal-fueled power plants, the generation of oil fly ash (OFA) in oil-fired power plants shows a high carbon content, but the recycling and reuse of OFA is much lower than with coal FA (CFA). Hogged fuel is widely used in north European countries and USA, where generate the most amount of wood ash (WA) worldwide. The average reuse of CFA is around 40% worldwide, less than 20% of OFA is currently being reused, and negligible amount of WA is recycled and reused (Pitman, 2006). The remaining is disposed into landfills, and is accompanied by a high cost of disposal, loss of valuable land, and the potential pollution of the soil and groundwater. Therefore, recycle, reuse and recovery of FA becomes important.

Unlike CFA, very limited research has been done on OFA and WA utilization. The focus has been on the recovery of such valuable metals as vanadium (V) and nickel (Ni). Research is also being proposed on the surface modification of carbon for flue gas desulfurization and NO_x, CO_2 adsorption (Yaumi et al., 2013, Davini, 2002). A small fraction of OFA is used as a filling in Portland cement; as a filler in polymers, asphalt, and cementitious materials; and as a stabilizing agent and adsorbent for wastewater treatment and solidification for waste and sludge (Shawabkeh et al., 2011). An important application of CFA is in concrete production, road basement material, waste stabilization/solidification, cement clinkers, amendments of soft soil, and, more recently, geo-polymers (Al-Degs et al., 2014). Due to the alkaline nature, WA has a potential being the amendment of acidic soil (Pitman, 2006). The elemental composite of WA is mainly Ca, K, Na and Mg. WA therefore can be used as a composting material (Pitman, 2006).

Two types of fly ash (FA) were used in this study: OFA from oil-fired power plants in Saudi Arabia to remove organic matter from intake sources and for oil spill cleanup, and FA from the Corner Brook Pulp and Paper (CBPP) mill for composting and stabilizing municipal sludge.

The OFA obtained from the Saudi Arabian power plants result from the burning of HFO and crude oil. The mixed fuels, fossil fuel (bunker C and waste oil) and renewable fuel (by-products from mill operation, such as bar and sawdust), are utilized in the CBPP boiler. Although they have entirely different characteristics, both types of ash have high levels of carbon, and the objective was to recover carbon from the waste and use it for technology development.

Currently, a full-scale municipal drinking water treatment plant could equip with multiple disinfection processes. Most commonly used disinfection technology Canada is chlorination, which uses sodium hypochlorite, liquid or gas chlorine as disinfectant due to its easy to operate, efficient, and low cost (Health-Canada, 2009). Due to the nature of high average TOC in water bodies, chlorination disinfection will lead to the formation of disinfection by products (DBP) (Chowdhury et al., 2011). Advanced technologies have been implemented, such as Ozone, UV, mixed oxidants (MIOX) and chloramine. However, these advanced technologies require higher costs and higher skilled operators. The economic concern and the lack of skilled operators make it infeasible to implement advanced disinfection system in small communities (Ling and Husain, 2014). Therefore, an easy to operate and cost effective water treatment system is urgently required in such communities and one such simple system is to introduce carbon filter barrier to remove TOC in the water system before chlorination.

Activated carbon is the most commonly used filtration media, it has high surface area, outstanding adsorption capacity to remove organic constituents and by adding AC in the water treatment system can eventually protect other treatment groups, such as membrane fouling (DeSilva, 2000). The raw materials have considerable influence on the characterization of final activated carbon products. The characteristics of some prevalent granular activated carbons vary a lot (DeSilva, 2000). The price of raw materials also varies. This prevents the implementation of commercial activated carbon filtration in rural areas.

Offshore oil spills during drilling or transportation have been a major concern of marine contamination (Karakasi and Moutsatsou, 2010). The most frequently utilized technologies to treat offshore oil spills are booms and dispersants. However, with the application of dispersants, an oil film is dispersed into small droplets and dissolved in the ocean water and the toxic components remain in the water columns and sediments. The new trend with the oil spill cleanup is to develop adsorbent and absorbent materials to remove both the floating and dissolved fractions with minimum environmental effects.

Carbon soot, zeolite, agriculture waste has been studied to develop cost effective, hydrophobic, high oil adsorption capacity carbonaceous materials. However, due to the nature of hydrophilic surface and low carbon content, generally 20-50%, these low-cost materials require additional chemical and physical treatment to make them suitable for oil spill cleanup. A low-cost material requiring least treatment is urgently needed.

Sludge, the main by-product in any wastewater treatment process, contains solid wastes from municipal, agricultural, commercial, industrial, and surface water (Werther and Ogada, 1999). The

sludge generated from wastewater treatment plants is always a serious environmental concern. Usually, after the dewatering process the remaining solids are compressed and disposed directly into the landfill. According to the official website of the City of St. John's (http://www.stjohns.ca/living-st-johns/city-services/wastewater-treatment), around 65 tons of solid waste are produced which end up in the landfill every day, occupying a large area of the landfill sites. Nearby communities complain about the unpleasant odour from this dewatered sludge.

There are three widely applied ways to manage and apply sludge: landfilling, incineration, and fertilizer or soil supplement (Chen et al., 2012, Werther and Ogada, 1999). In many developing countries, treated sludge is dumped directly into the sea (Werther and Ogada, 1999).

Landfill is the most favored method to treat sludge due to its low-tech requirement. Municipal sludge can be dumped to landfill by mixing with other waste to save space and cost (Chen et al., 2012; Werther and Ogada, 1999; Yoshida, 2013). However, odour, landfill leachate, natural gas emission and closure at the end of life remain the concern.

Incineration is other generally used technology to treat municipal sludge. By high temperature heating, sludge and other waste can be converted into ash, thus greatly reducing the volume of the waste. However, during the incineration process, it may release hazardous gases and fine particles into the air causing air pollution and health problems (Schetter, 1989). An environmental friendly and easy to operate technology is therefore needed to reduce the impact of the sludge on the environment by composting with fly ash.

1.2 Scope of the Research

The main objective of this study is to convert FA into a valuable resource and reduce its volume significantly by extracting unburned carbon, which constitutes a significant portion of waste residue. It is proposed to use recovered carbon for various beneficial uses:

(a) to develop an affordable adsorbent to reduce DBPs in drinking water;

(b) as a cost-effective and environmentally safe product to remove hydrocarbons during an offshore oil spill; and

(c) to improve municipal sludge as a composting product.

1.3 Overview of the thesis

To accomplish objectives, two types of ash were used: OFA from power plants using crude oil and HFO, and FA generated by burning wood chips and biomass in a boiler. The findings of this research and the methodology are reported in various chapters of the thesis.

Chapter 1 provides background information on FA and Chapter 2 describes the physical, chemical, and mineralogical characterization of OFA. Chapter 3 discusses the leaching methods for recovering clean carbon and the efficiency of removal of impurities. Chapter 4 discusses methods for activating carbon. In order to conduct a batch test on TOC removal and a performance assessment of carbon filtration to reduce DBPs in drinking water, a design of experiment concept was applied to assess TOC and DBP removal in water-supply systems. The application of OFA as an absorbent in an offshore oil spill cleanup is covered in Chapter 5, and Chapter 6 discusses the methodology and experimental work of FA in municipal sludge composting and stabilization. The findings of the research and recommendations for future studies are summarized in Chapter 7.

The American Society for Testing and Materials (ASTM) methods were utilized in FA physical characterizing, total carbon content gives the overview of the sample non-metallurgic composition and indicates the existence of high quality carbon, and particle size distribution, SEM, XRD, and FTIR give information at micro level for sample composition, structure, and crystal phase. The XRD pattern indicates that FA carbon exists in the form of graphite. BET surface area analysis shows the low original surface area and its improvement by different treatment and activation methods.

FA was treated by acid, water, and alkali to find the best metal leaching method. By testing different leaching times, a four-hour leaching was found to have the best performance. Recycling residue acid with the supplement of fresh acid was also tested to identify the potential of economically cleaning the FA.

Batch test and optimization analysis were performed to determine the significant factors in using OFA as the adsorbent in TOC removal. In the application of oil adsorption, high oil adsorption capacity and relative low hydrophilic was found by utilizing a thermogravimetric analysis (TGA). CBPP FA was applied in municipal solid waste composting; however, it shows very slow or no maturity process. A positive result was obtained in PAH degradation.

Chapter 2. Characterization of Fly Ash

Physical, chemical, and mineralogical analysis of both types of FA: OFA from power plants and FA from CBPP) was conducted using the approved standard methods in the literature as described in this chapter. All samples were measured duplicates for quality control and the average were reported.

2.1 Methods and Materials

2.1.1 pH

A pH meter was used to test the pH of OFA samples and followed ASTM D1512-05 (ASTM, 2012). Four grams of OFA sample was added to 50 ml of boiling deionized water and boiled on a heating plate for four minutes; it was then cooled to the ambient temperature. A pH meter analyzed the pH at the contact surface of the water and OFA slurry. The test was done in triplicate and the average value is the pH of the sample.

2.1.2 Moisture content

Moisture content was determined by following ASTM D2216-10 (ASTM, 2010). A crucible was burned in a muffle furnace at 650℃ for one hour to remove organic matter, and then cooled in a desiccator and the crucible weighed and the weight recorded. Two $\pm$ 0.1 g of OFA sample was weighed in the crucible and placed in a conventional oven at 110 $\pm$ 5℃ for overnight. The crucible and sample were weighed together until there was no change of weight. All samples were analyzed in triplicate and the average calculated as the moisture content of the samples. The moisture content can be calculated as

$$M\% = \frac{w_{raw} - w_{dry}}{w_{raw}} \times 100\% \quad (2\text{-}1)$$

where:

M%: moisture content in W/W%

w_{raw}: weight of raw sample

w_{dry}: weight of the sample after drying

2.1.3 Ash content

The OFA sample was first dried at 110 ± 5℃ in a conventional oven overnight to remove the moisture. A crucible was burned in a muffle furnace at 650℃ for one hour, then cooled to ambient temperature in a desiccator and weighed (ASTM, 2013). The dried sample was then weighed for 2 ± 0.1 g and transferred to a crucible and placed in a muffle furnace at 650℃ for 16 hours. All samples were analyzed in triplicate and the average calculated as the ash content of the samples. The ash content can be calculated as

$$M\% = \frac{w_{ash+crucible} - w_{crucible}}{w_{dry}} \times 100\% \quad (2\text{-}2)$$

where,

M%: ash content in W/W%

w_{dry}: Weight (g) of dried sample

$w_{ash+crucible}$: Weight (g) of ash after burning

2.1.4 Density

Bulk density analysis followed ASTM D7481-09 method (ASTM, 2009). Weigh a certain weight of FA and transferring it to a 15 ml cylinder to measure the volume. The density can be calculated by the formula

$$\rho = \frac{w}{v} \quad (2\text{-}3)$$

Where,

ρ: Density (g/cm^3)

w: weight (g) of FA sample

v: volume (cm^3) of FA sample

2.1.5 Particle size distribution

Particle size distribution was analyzed by a Laser Diffraction Scatter analyzer (Horiba LS-950). The OFA sample was placed in the analyzer pool, allowed to evenly suspend in the distilled water, and the particle size measured.

2.1.6 Total carbon content

The OFA sample was dried in a conventional oven at 105 ± 10˚C for 24 hours to remove the moisture, and then 2 ± 0.1 mg was weighed in a tin capsule by a microbalance. The weighed sample was analyzed by a CNH analyzer (Perkin Elmer, Perkin 2400) at CREAIT lab. The result is given in both exact weight and percentage of carbon.

2.1.7 Scanning electron microscope (SEM) analysis

Surface morphology and point elemental analysis was conducted by an SEM (Phenom Pro). A sticky pad was placed on a pin and a thin layer of the OFA sample spread on the pad and homogenized by spraying compressed air to remove additional layers of the sample. The pin was then transferred to the sample holder and inserted into the instrument for analysis.

2.1.8 BET surface area

The surface area (m^2/g) was measured from the adsorption isotherm by the Brunauer, Emmett and Teller (BET) equation (Equations 2-4 to 2-8), using a relative pressure range of 0.05-0.35, considering that the area of the N_2 molecule is 0.162 nm^2 at 77K (Reinoso et al., 1997). The total pore volume, V_T, was obtained from the N_2 adsorption isotherm at $p/p_0 = 0.99$.

$$\frac{1}{v\left(\frac{P_o}{P}-1\right)} = \frac{1}{v_m c} + \left(\frac{c-1}{v_m c}\right)\left(\frac{p}{p_o}\right) \tag{2-4}$$

$$v_m = \frac{1}{S+I} \tag{2-5}$$

$$c = 1 + \frac{S}{I} \tag{2-6}$$

$$SA_{BET} = \frac{(v_m N A_{(N)})}{v} \tag{2-7}$$

$$S_{BET} = \frac{SA_{BET}}{a} \tag{2-8}$$

where, v = volume of adsorbed N_2 gas at standard temperature and pressure (STP), P and P_0 are the equilibrium and saturation pressures of the adsorbate, v_m = volume of gas (STP) required to form one monolayer, c = BET constant related to energy of adsorption, N = Avogadro's number (6.02E+23), $A_{(N)}$ = cross section of N_2 (0.162 nm^2), SA_{BET} = total BET surface area (m^2), S_{BET} = specific BET surface area (m^2/g), and a = mass of adsorbent (in g). The BET surface was calculated from the BET equation by plotting $1 / v\,[(P_0 / P) - 1]$ on the y-axis and P/P_0 on the x-axis in the range of $0.05 < P/P_0 < 0.35$. The slope (S) and the y-intercept (I) of the plot were used to calculate v_m and the BET constant c.

One important index of the capability of physical absorption is the specific surface area. A higher surface area indicates a better adsorption capability. A nitrogen (N_2) adsorption isotherm curve is one of the more commonly used methods for surface area analysis. Industrially, an iodine test is the general method used to determine the surface area of AC. A methylene blue test is utilized to analyze the mesopore volume of AC. In this study, a TriStar II Plus micrometric analyzer was utilized to determine the surface area and the pore distribution of the OFA samples, which were first heated at 120°C for two hours for the degassing procedure. Then 500 mg of the sample was weighed and analyzed under different pressure levels.

2.1.9 Trace and heavy metals analysis

Heavy metals in the OFA samples were digested by modified EPA method 3050 (EPA, 1996) and analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Elan DRC II) at CREAIT lab. One hundred milligrams ± 10 mg of the OFA sample was weighed and placed in a 15 ml Teflon vial (Savillex) with a screw cap and the weight of the vial recorded. Three milliliters

of 8N nitric acid (HNO_3) was added to the vial and heated on a heating plate at 70˚C for two days. The vial cap was tightly closed to reflux acid and generate pressure to speed up digestion. The samples were then dried and cooled and 1 ml of HNO_3 and 1 ml of hydrogen peroxide (H_2O_2) added to the system and heated at 70˚C for two days to remove organic matter. The samples were again dried and cooled. An additional 2 ml of 8N HNO_3 and 1 ml hydrofluoric acid (HF) were added to the samples, which were heated at 70˚C for two days. After drying and cooling, 3 ml of aqua regia (V_{HCl}: V_{HNO3}= 3:1) was added to the sample and heated at 70˚C for one day. The sample was then dried and cooled and dissolved in 2% HNO_3. All of the solution was transferred to a 50ml conical centrifuge tube and deionized water added to 45 g. The solution was then filtered by a 0.45 µm syringe filter. Then 0.5 g of the solution was transferred to an 11ml tube and deionized water added to 10 g, and analyzed by an Elan DRC II ICP-MS analyzer.

2.1.10 X-ray diffraction (XRD)

Phase analysis was conducted by a Rigaku Ultima IV x-ray diffractometer with a copper x-ray source and a scintillation counter detector. Samples were placed in a clear sample container.

2.1.11 Sieve analysis

An OFA-1 sample was sieved for 36, 44, 63, 90, and 125 µm to find the weight distribution by size. One kilogram of the OFA-1 sample was placed in a coarse sieve and shaken for one minute. Samples were collected and weighed by each size intervals.

2.1.12 Fourier Transform Infrared Radiation (FTIR)

Functional groups on the OFA sample surface were analyzed by FTIR to present the differences after acid, water, alkaline treatment and before and after activation. The analysis was performed in transmittance mode with the wavenumber from 4000 to 500 cm^{-1} by Bruker Alpha E spectrometer. Attenuated total reflectance (ATR) method was initially applied with a single bounce diamond reflection; however, due to the high carbon content, no significant peaks could be found.

A potassium bromide (KBr) pellet technique was applied to increase the sensitivity of the analysis. First, 200 mg of dried KBr was weighed in a dry glass container, then 1 mg of the OFA sample was weighed in the same container. Second, the mixed sample was transferred to a mortar and pulverized to homogenize it. Third, the homogenized sample was transferred to a KBr holder and pressed under a 10-ton vacuum hydraulic compressor to form the plate. Last, the plate was placed in a plate holder and analyzed by OPUS software.

2.2 Results and Discussion

2.2.1 pH, moisture content, ash content, particle size distribution, and density

The results of the characterization of the OFA-1 and OFA-2 samples are summarized in Table 2-1. Both samples are highly acidic and have entirely different pH values than the CFA and WA. Generally, the pH values of CFA and WA are highly alkaline, from 8 to 12; OFA-1 and OFA-2 have acidic pHs, 2.3 and 1.9 respectively. Navarro, et al., (2007) illustrated that the valent of V in OFA is mainly four valent, which is the high water soluble form (Navarro et al., 2007). Direct disposal of OFA into a landfill could possibly cause transition metals (such as V) leaching into the soil and further contaminate the groundwater. The moisture content in these two samples is

relatively low: 0.3% and 1.98%. The ash content of OFA-2 is much higher (21.65%) than that of OFA-1 (0.91%). The unburned carbon in OFA-1 is about 90%; in OFA-2, it is only 56% by weight. The high ash and low carbon content could be due to the different burning technologies and efficiency. These two parameters also indicate a high concentration of heavy metals and the other impurities of OFA-2 (see Table 2-2). The particle size distribution of OFA-2 is shown in Figure *2-1*; the mean size is 134.01μm, and the particle size is relatively evenly distributed from 15.6 to 250 μm.

Table 2-1 Characterization of OFA-1 and OFA-2

Sample	pH	Moisture content (%)	Ash content (%)	Carbon content (%)	Density (g/cm^3)	Mean particle size (μm)
OFA-1	2.3	0.3	1.4	90.1	0.31	108
OFA-2	1.9	1.98	21.65	56.2	0.35	135

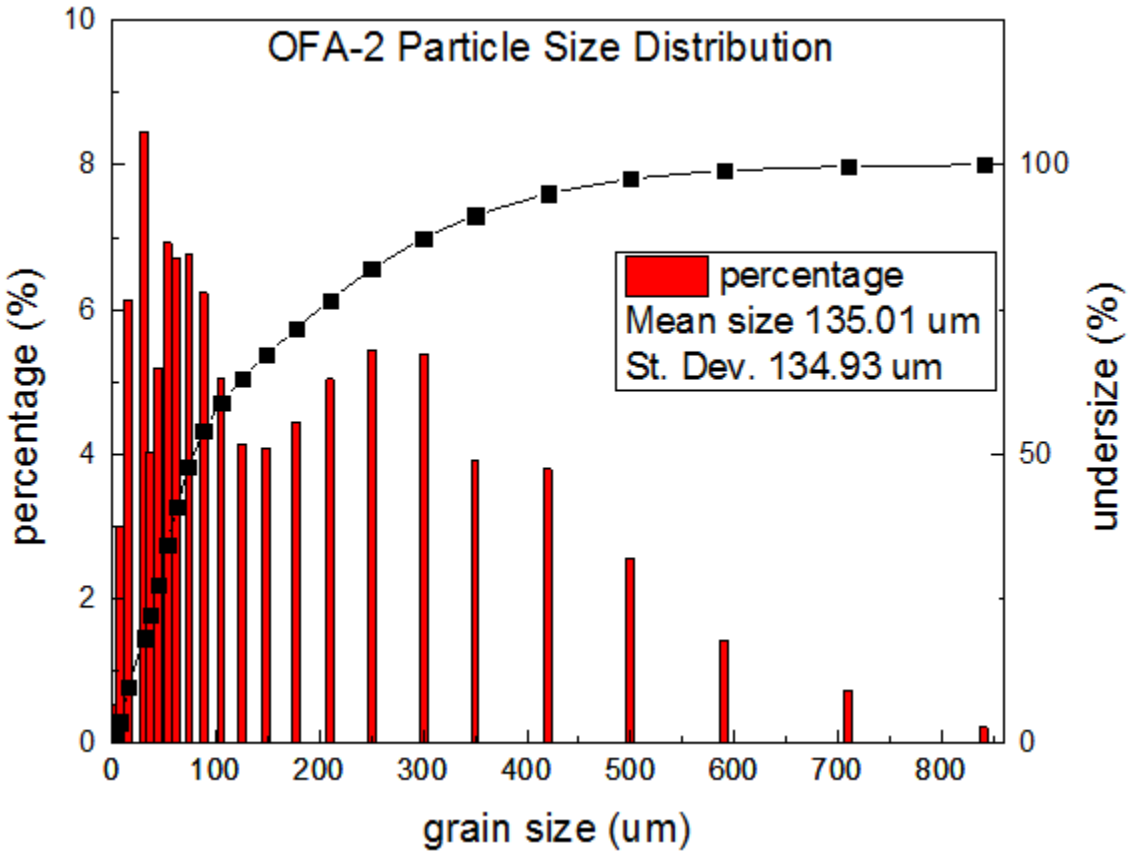


Figure 2-1 Particle size distribution of OFA-2

2.2.2 Trace and major metal content

Trace and heavy metals are reported in Table *2-2*: the metal content of OFA-2 is much higher than that for OFA-1. This matches the higher ash content of OFA-2. The metal content of OFA-2 is much higher than that in OFA-1. The concentration of V in OFA-2 is 20 times higher than that in OFA-1: 17,085 mg/kg or 1.71% by weight, which is higher than that in the ores being processed for V recovery. If an ore has 0.5% or more V by weight, it is considered to be economical to process and recover (Kerr et al., 2013). A high concentration of Ni is also found in OFA-2. The

British Geological Survey illustrates that if Ni in the ore is 0.2% to 3% it is economical to process (Survey, 2008). Since the Ni level in OFA-2 is 8182 mg/kg, which is equivalent to 0.8% by weight, it is economical to recover Ni from the OFA-2 samples.

Table 2-2 Trace and heavy metals of OFA-1 and OFA-2

Sample	OFA-1	OFA-2
Unit	mg/kg	
Mg	2125.805	15266.67
Ca	964.484	2418.1
V	717.598	17085
Ni	417.869	8182
Fe	795.443	6741.8
S	10147	55015
Cr	5.056	32.617
Al	541.958	2084.59

2.2.3 XRD pattern

XRD analysis is a technique utilized to analyze material crystal phase and elemental composition. In this study, XRD analysis was applied to determine the elemental composition. The XRD results of raw OFA, acid cleaned OFA and commercial graphite are shown in Figure 2-2 and Figure *2-3*.

Due to the high component of carbon, a large graphite peak can be found at 2θ=26˚ of all XRD patterns of FA samples. The peak occurred at 2θ=15° is the peak of $Mg_2V_3O_8$. This is due to the additive of MgO when burning HFO to prevent corrosion of boiler turbine. After acid treatment, the $Mg_2V_3O_8$ peak disappeared, this is due to the soluble four valent vanadium dissolved in acid. The XRD patterns of FA indicate that there is no difference in crystal phases but there are some differences in intensity. The highest intensity of graphitic carbon was obtained from acid-recovered carbon; the lowest, the raw sample. This could because acid leaching and crushing can break FA into finer size particles and give a better x-ray diffraction. As raw FA is much coarser than crushed or cleaned FA, the intensity of the XRD result is lower than with crushed or cleaned FA. The higher the intensity, the higher purity the graphite has, and the sharper the peak is, the higher degree the graphitization is. Compare with CFA, and WA, OFA contains very high graphitic carbon content.

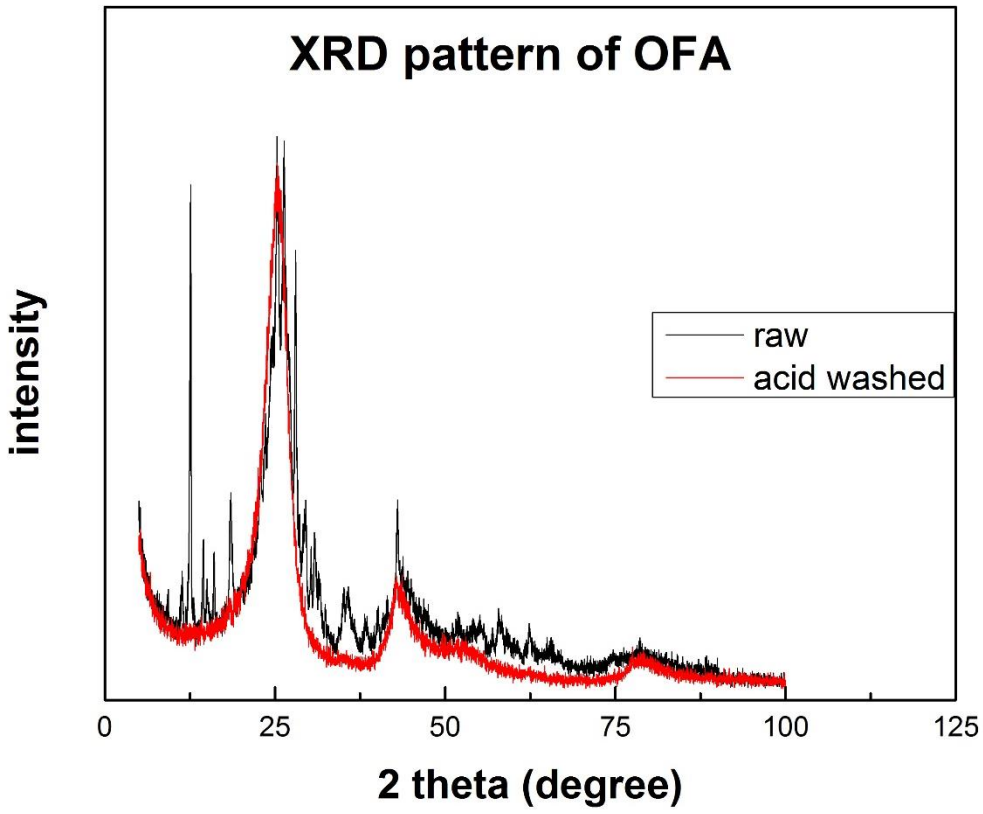


Figure 2-2 XRD pattern of OFA

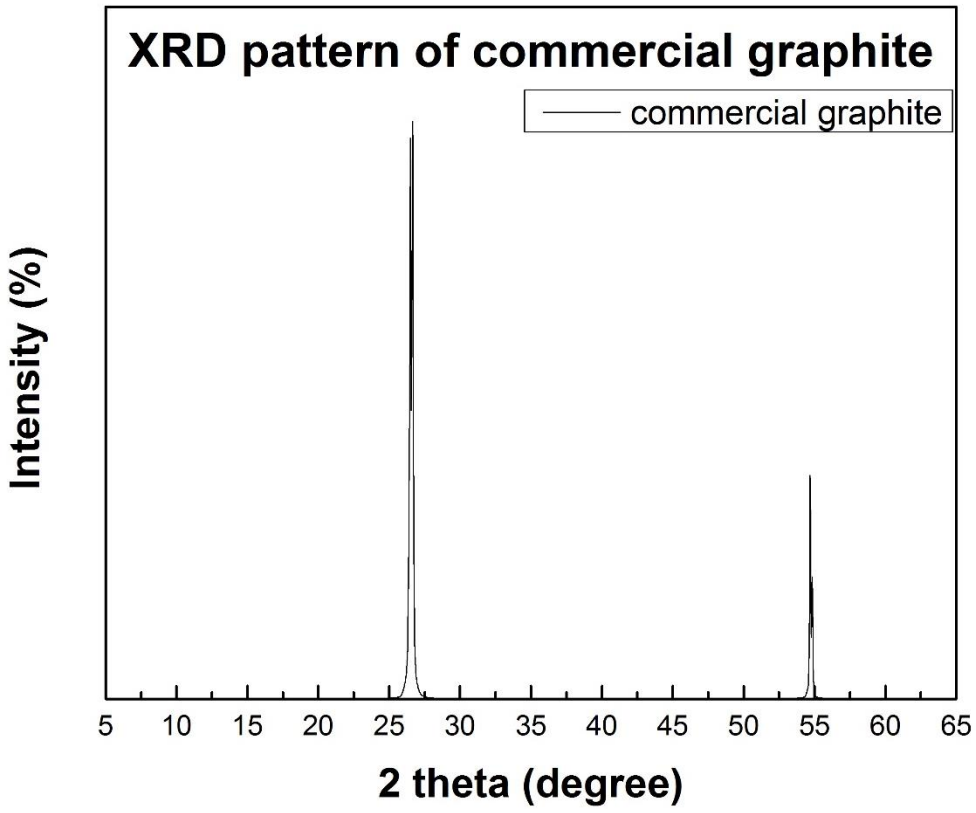


Figure 2-3 XRD pattern of commercial graphite

2.2.4 SEM analysis

Particle morphology, size distribution, and pore structure can be analyzed by SEM, and from this analysis, spherical and amorphous particles can be observed from both OFA samples. The surface of OFA samples are draped shape and the main contents are carbon and sulfur.

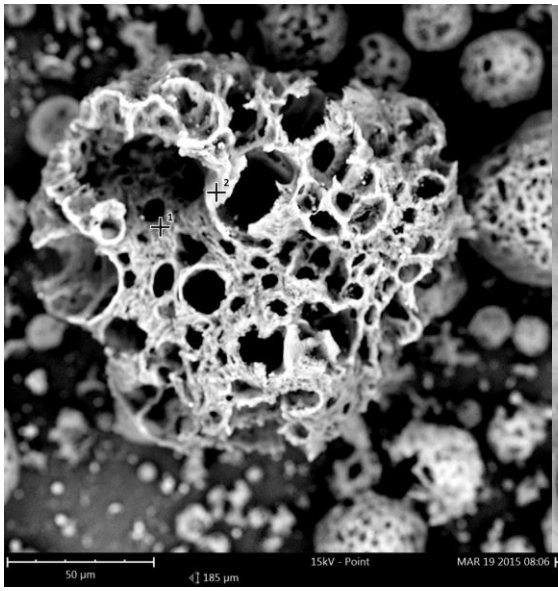


Figure 2-4 SEM of AC-OFA

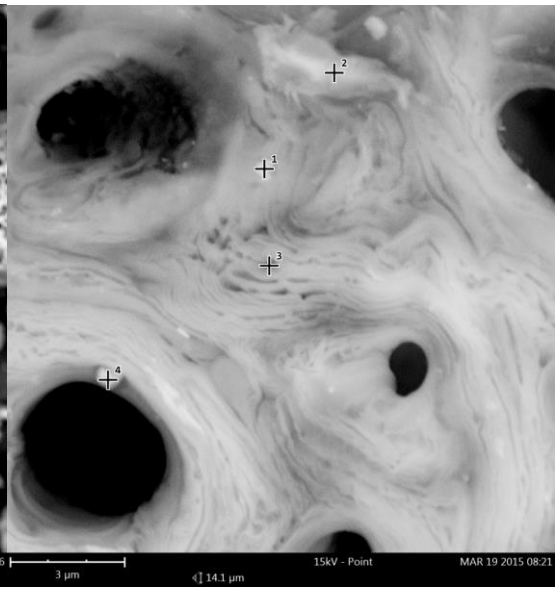
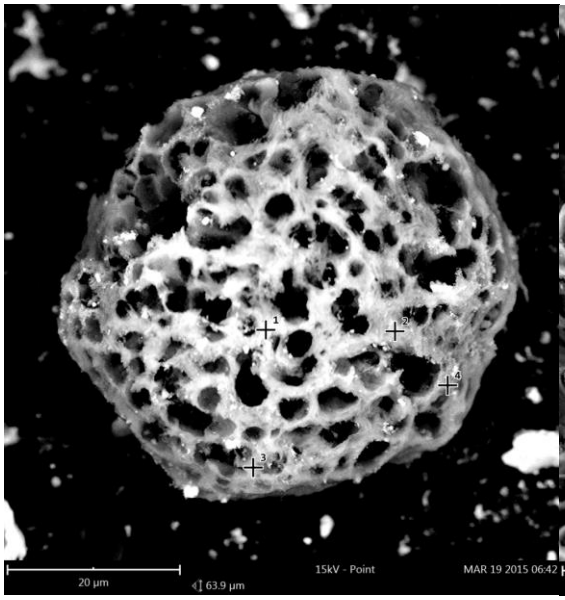


Figure 2-5 SEM of raw OFA surface

After acid washing and activation, the major elements left on the particle surface are C and S. Due to acid washing, the metals attached to the particle surface can be removed, more mesopores can be developed, and, after activation, when the carbon is burned off, only a skeleton of the spherical particles remains.



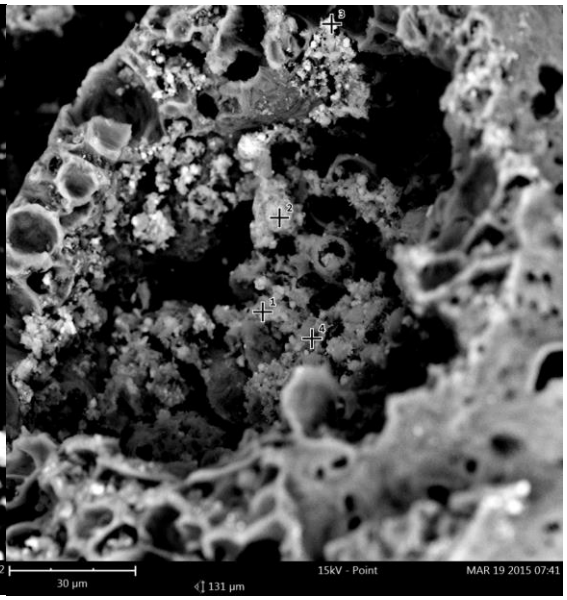


Figure 2-6 1N NaOH treated AC-OFA Figure 2-7 1N NaOH treated OFA

The particle size of the OFA is smaller than that of the raw samples, due to the breakage of the Al-Si-O groups. Immersed in hot NaOH solution, SiO_2 on the surface of the OFA samples can be easily dissolved and rebound. The texture of the NaOH-treated OFA is more glass-like than the acid treated. After NaOH treatment, most metal oxides remain in the OFA particles but are more exposed due to the breakage of the surface binding. Those exposed metal oxides may contribute to a catalytic effect during activation and the potential to be converted to a catalyst for oxidation-enhanced degradation, such as the Fenton process. A section image of OFA-2 treated by 1N NaOH shows a hollow space inside the FA particle, and different metal oxides filled inside the sphere as shown in Figure 2-7.

Figure 2-8 SEM of AC-OFA-2 NH_3H_2O treated

2.2.5 Surface area

Raw, acid-washed, and activated samples were analyzed for BET surface area (Brunauer, Emmett, and Teller, 1938); the results are listed in Table *2-3*. Due to high impurities, the surface area of the raw material is relatively low (2 m^2/g). After acid leaching, the surface area increased to 12 m^2/g; after physical activation, it increased to only 20 m^2/g. Although the OFA samples after activation have a 10-fold increase in surface area relative to that of the raw materials, compared with commercial AC, which usually has a surface area in the range of 800 to 1000 m^2/g, the surface area of activated OFA still requires improvement.

The results of pore volume and pore size indicated that none of the OFA samples has micropores. This could be due to the horizontal fixed heating tube used for OFA activation. As the OFA placed in this tube cannot be rotated, there was not enough contact area for the OFA samples. Only the

upper layer is in contact with the CO_2.

Table 2-3 BET surface area of OFA-2 and crushed OFA-1

Sample	BET surface area (m^2/g)	Pore volume cm^3/g	
		Microspores	Mesoporous
Raw	2	ND	ND

2.2.6 FTIR

FTIR analysis provides the view of surface functional groups, which can provide the potential possibility of binding, surface chemical characterization of carbon. This will also check if there are any functional groups attached to or detached from the ash surface before and after treatment or activation. In water and wastewater treatment process, the result of FTIR can be used as the interpretation of adsorbent surface charge, surface polarity and ionic or non-ionic. OFA samples were examined from 500 cm^{-1} to 4000 cm^{-1}. The results of all samples are presented in Figure 2-9.

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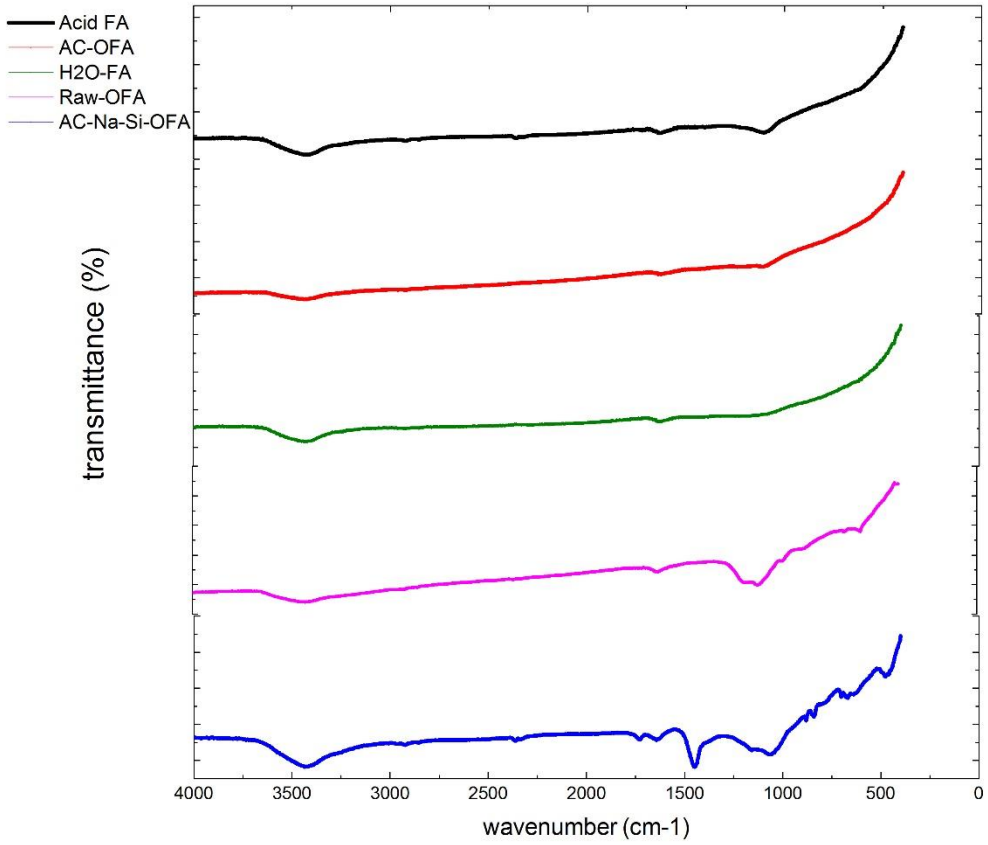


Figure 2-9 FTIR of treated and raw OFA

The broad peak between 3600 cm^{-1} to 3000 cm^{-1} indicates the existence of hydroxyl stretching belongs to either free -O-H or -COOH groups, which was the result of oxidation during burning in the power plant. Two small peaks occur at 2922 cm^{-1} and 2853 cm^{-1}. In the range of 2800 to 2950 cm^{-1}, they correspond to the stretching of alkyl C-H. Because alkane C-H bonds is commonly existing in most carbon materials, therefore it is negligible in surface modification. The broad peak observed between 1700 cm^{-1} and 1500 cm^{-1} corresponds to the aromatic C=C bending. The minor peak at 2357 cm^{-1} corresponds to CO_2. The minor peaks observed at 1115 and 1046 cm^{-1} are C-O groups. The sharp peak at 1449 cm^{-1} of the Na-Si modified AC could be assigned to the alkyne

groups. The small peak at 1727 cm^{-1} could be a C=O group. The broad peak at 1064 cm^{-1} could be due to the stretching of CO, CCO, and CC. The two peaks that appeared in the range between 1630 and 1850 cm^{-1} could be assigned to either anhydride carbonyl groups or different types of carbonyl groups.

2.3 Summary

The physical and chemical properties of OFA-1 and OFA-2 show their acidic nature and the potential of leaching to an extent by water and acid rain when being landfilled. This could cause corrosion of the soil and surrounding vegetation, since most vegetation favour soils with a pH around 8. Both samples were dry in nature, because of the low moisture content. The ash content of OFA-1, much lower than that of OFA-2, indicated a higher efficiency of boiler in the plant. This also indicates that it is economical to recover valuable metals from OFA-2 ash. Both samples have relatively coarse particles, as determined by particle size distribution, SEM analysis, and sieve analysis. The XRD analysis confirmed the high carbon content of OFA-1 and the relatively lower carbon content of OFA-2. OFA-2 shows a more complex XRD pattern. The FTIR result shows that both OFA samples contain a -COOH group which is the indicator of both samples being evenly dispersed in asphalt as a colour additive.

Chapter 3. Treatment of Oil Fly Ash

3.1 Introduction

All types of FA are the residue of burning, or incineration of heavy fuel oil, crude oil, waste materials, or municipal wastes. More or less, certain elements (such as Mg, Ca, V, Cr, P and Cl) could be accumulating after burning. Research has been conducted on the extraction and recovery of valuable metals from FA. Acid leaching is the general method for treating FA. Hydrofluoric acid may be used to remove Si in CFA due to the high SiO_2 content, while acid leaching has been widely utilized for OFA treatment.

3.2 Carbon Recovery

Carbon recovery technology varies because of the different characterization of each FA sample. CFA has a high pH, SO_2, Ca ions, and extremely fine particle; OFA is highly acidic and has almost no Si existing in matrices. The major treatments of OFA samples are acid, water, and NaOH leaching. Acid leaching will equally dissolve all metals into solution, while NaOH will be more specific for certain metals, such as Mo and V. Because of the low pH values of the OFA samples, adding fresh water can also leach metals from them.

3.2.1 Acid treatment

Acid leaching process was modified from Mofarrah's method (Mofarrah et al., 2014). Ten grams of OFA sample was weighed and transferred into a 500 ml beaker, 60 ml of 1.5N H_2SO_4 added to the beaker, and the beaker placed on a heating plate for one to four hours to leach the metals. Acid recycling was applied to perform a cost-effective metal-leaching procedure. A parallel comparison

experiment was conducted to compare both the recycling performance of OFA-1 and OFA-2. Two groups of experiments were performed under the same conditions; one group of samples was covered by watch glasses, another connected to a reflux condenser tube with anhydrous chloride calcium ($CaCl_2$) to prevent acid evaporation. Both Each samples of 10 g each was put in a 500 ml glass beaker, mixed with 60 ml 1.5N H_2SO_4 at 80˚C, and stirred on a heating plate with a magnetic stirrer for one and four hours. After filtration, the acid solutions were measured in a 100 ml cylinder and the remaining volumes recorded. The collected acid was reused for fresh sample leaching with the addition of fresh acid to make up the total acid volume to 60 ml. The residual acid volume was recorded each time, then OFA samples washed by 500 ml of deionized water to remove the acid and the impurities. This cycle was repeated five times to leach the OFA-1 and 11 times for the OFA-2.

Carbon recovery technology varies due to the distinct characteristics of each OFA sample. CFA has a high pH, high sulfate (SO_4^{2-}), and calcium (Ca), and extremely fine particle sizes. OFA samples are highly acidic, with almost no silicon (Si) in the matrices. The effective treatment methods for extracting carbon from OFA samples are acid leaching, washing with hot water, and NaOH leaching. Acid leaching equally dissolves most of the metals into solution; NaOH is more specific for certain metals, such as molybdenum (Mo) and V. Because of the low pH values of the OFA samples, adding fresh water can aid in leaching metals from them. Single-stage acid washing was applied in this study.

3.2.2 Result and discussion

Carbon cleaning results are shown in Figure 3-1 to Figure 3-7. Figure 3-1 to Figure 3-3 show the results of metals resided in OFA by one hour and four hour leaching at different acid recycling time. Figure 3-4 and Figure 3-5 compare the results of reused acid on OFA-1 leaching times of one and four hours: Ni, V, and Zn accumulate in the acid solution, the metal removal rate is relatively stable, and after three reuses of acid, a longer leaching time results in a better leaching. The removal rate of V ranged from 83.3% to 93.2%; the removal rate of Ni reached 75% to 81.5%. The highest removal rates occurred with four-hour leaching trials.

Figure 3-6 shows the recycling of acid and fresh water in the leaching of the OFA-2 sample. The highest V removal rate of 91.7% occurred in the first washing. From the second to the tenth recycling of the same water, the concentration of V was very stable, around 2200 ppm. Navarro et al. (2007) illustrated that although no official documentary about the valent of V in OFA, mostly, it exists in OFA as four valent (Navarro et al., 2007). The high V removal rate by both water and acid could due to the high solubility of four valent V in water. Fresh acid leaching of Ni reached 76.6% removal, remaining stable at 75% from the second to the tenth recycling. The preliminary analysis shows that the recycling and reuse of acid with supplementary fresh acid can achieve results close to those with fresh acid. Due to its high initial concentration and the high leachability of V and Ni and relatively low carbon content, OFA-2 could be a valuable resource for metal recovery.

Figure 3-6 compares the concentrations of metals remaining in FA after 11 recycles of acid. Magnesium (Mg) showed 90% leaching by acid wash, and the leach efficiency shows no significant difference from recycled acid.

Figure 3-7 compares the leaching results of water and acid. Although due to the acidic characterization, after adding OFA, the water solution will be acidic with a pH of 1.9, the leach ability is much lower than acid does.

Ognyanova et al. (2009) studied metal extraction from spent catalysts. In addition to roasting samples to recover metal oxides, the optimum leaching condition was confirmed for metal extraction from complex matrices of metals (Ognyanova et al., 2009). The optimum condition for V leaching also shows that H_2SO_4 concentration will not affect leaching efficiency, but contact time has a positive effect on V leaching and negligible effect on Ni leaching. A high acid to solid ratio may have a negative effect on metal leaching; however, more in-depth study is needed.

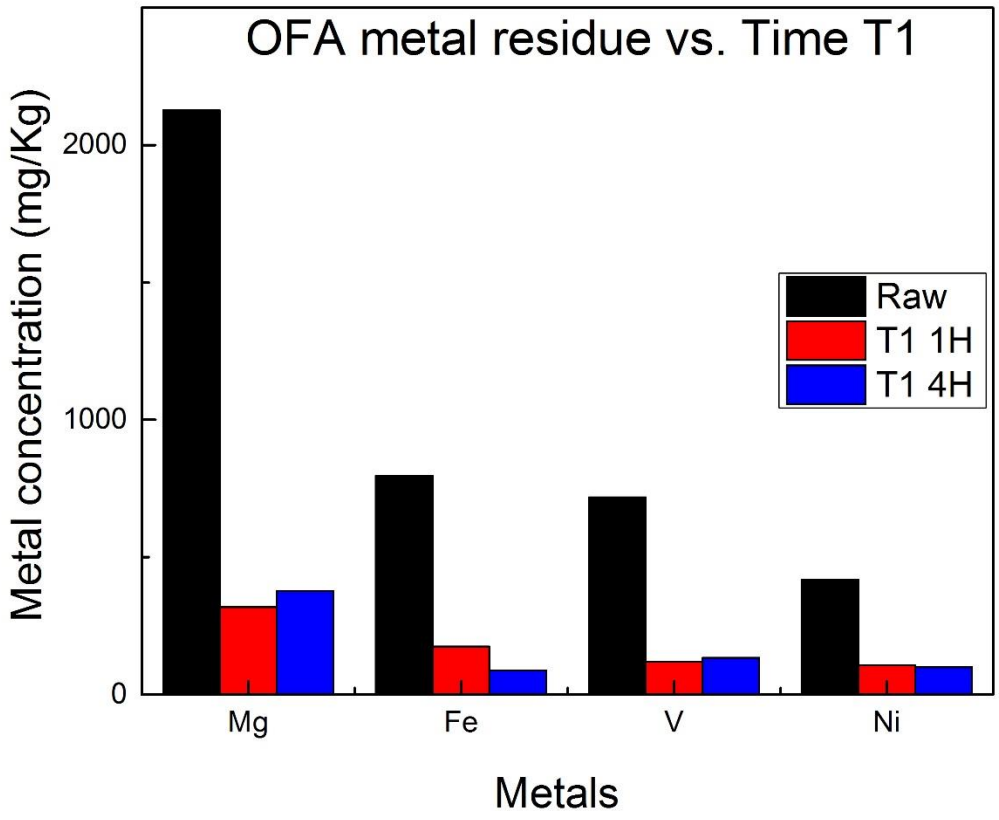


Figure 3-1 Metal residue after T1

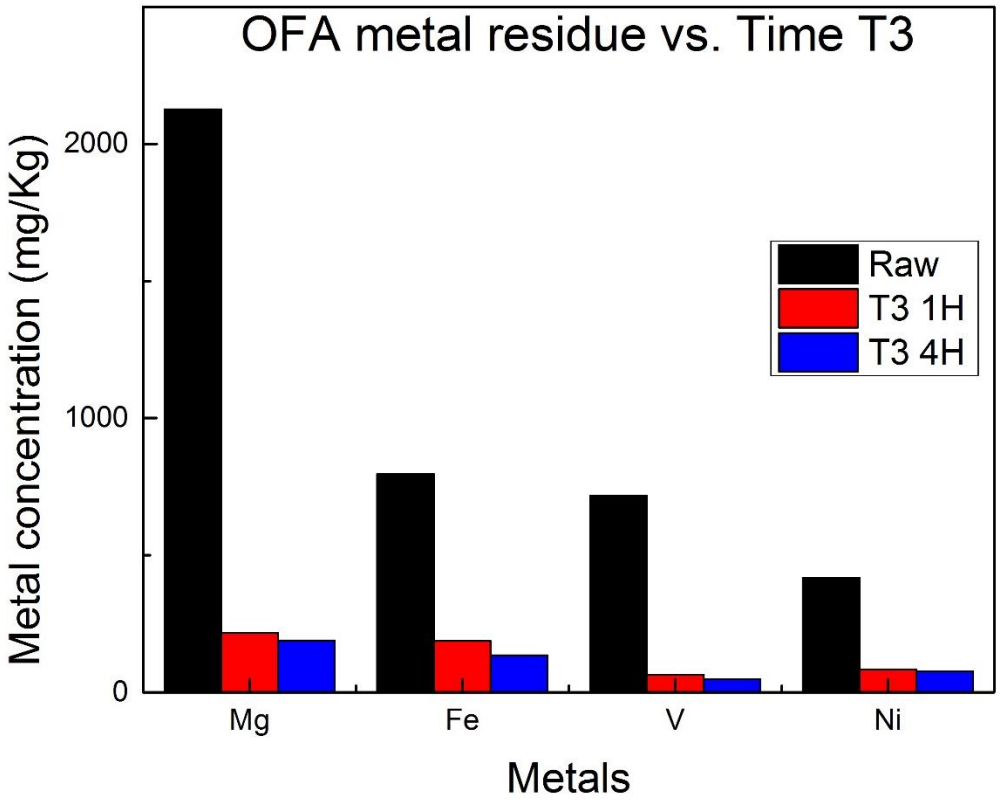


Figure 3-2 Metal residue after T3

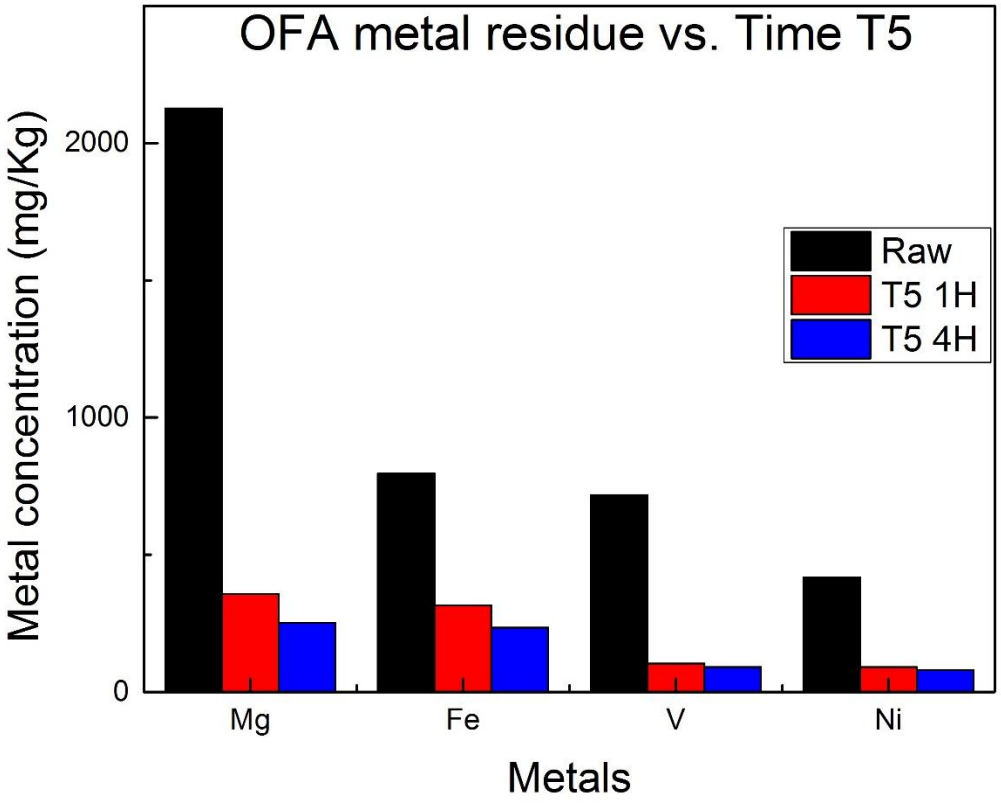


Figure 3-3 Metal residue after T5

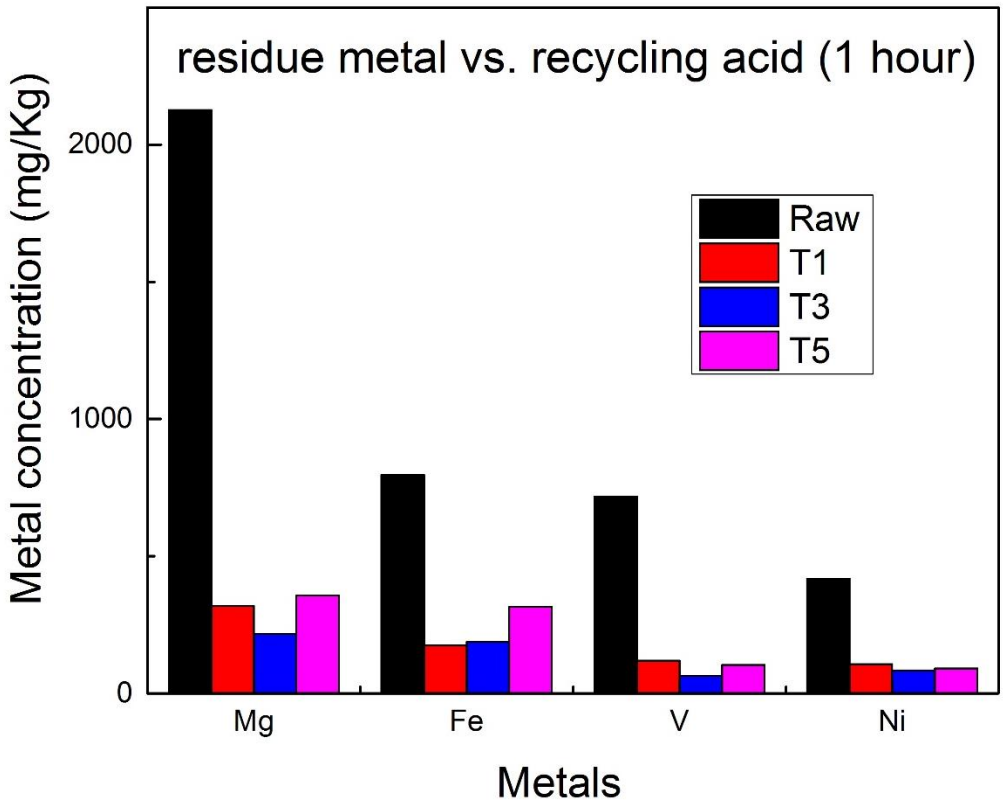


Figure 3-4 1-hour leaching efficiency by recycling acid of OFA-1

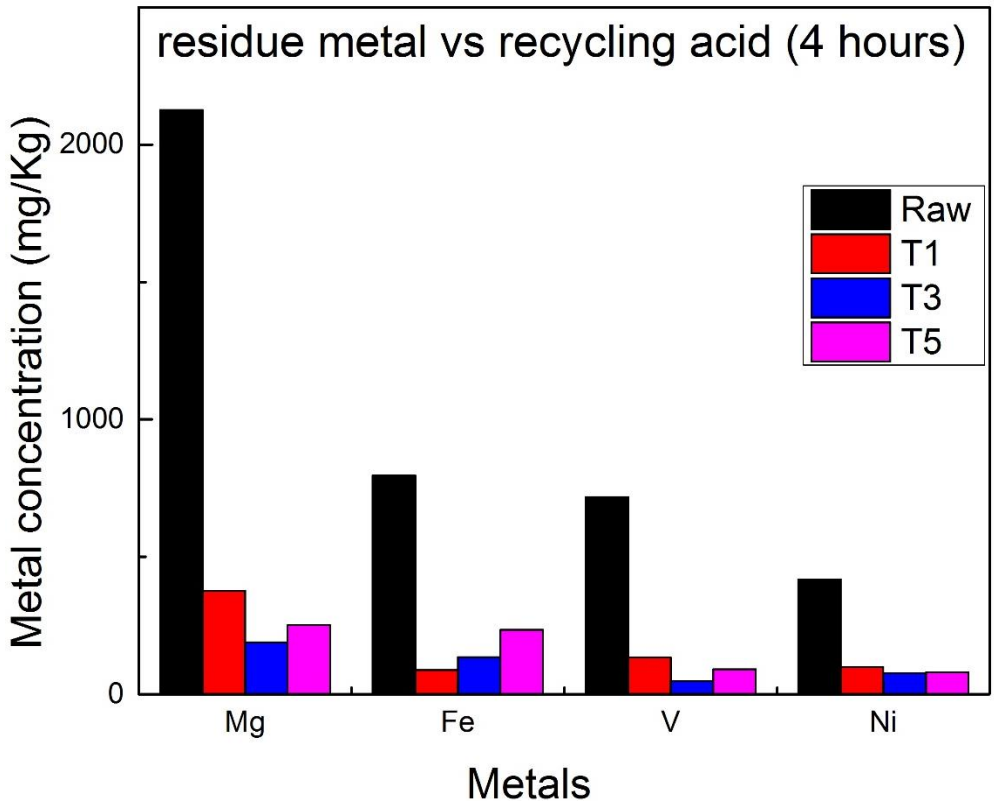


Figure 3-5 4 hour leaching efficiency by recycling acid of OFA

Where,

Raw is the concentration of metals in OFA-1 as received;

T1 is first leaching with fresh acid leaching for 1 and 4 hours;

T3 is the third leaching using recycled acid with supplementary fresh acid;

T5 is the fifth leaching using recycled acid with the supplement of fresh acid.

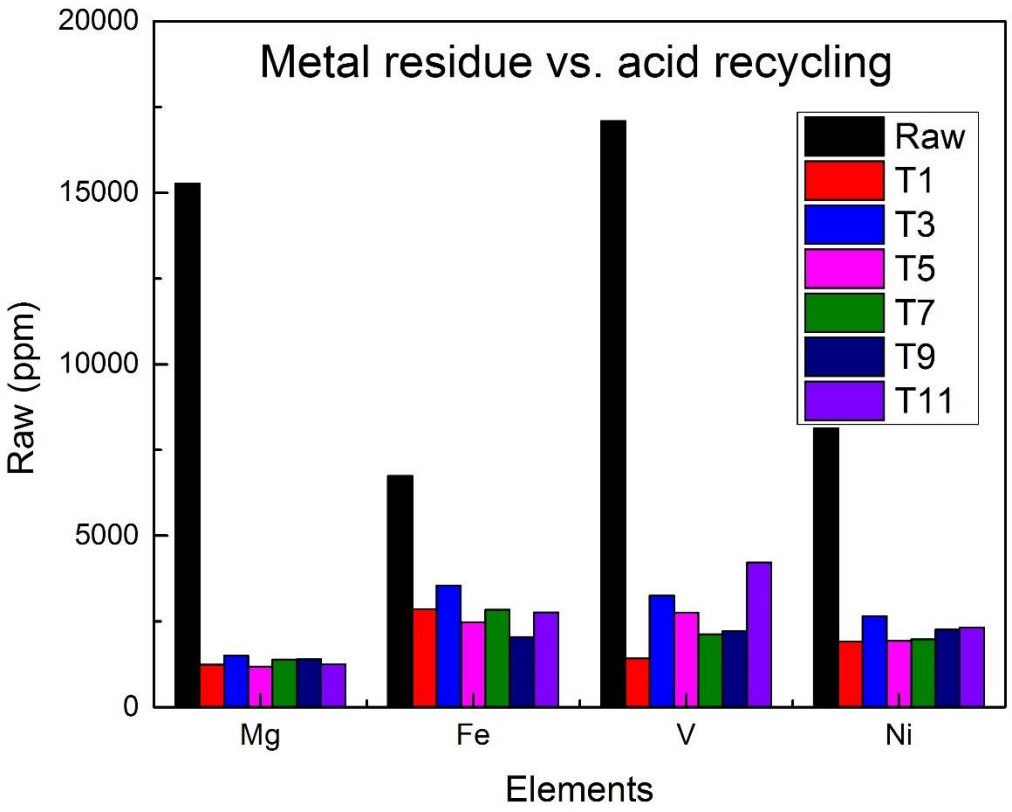


Figure 3-6 Metal leaching efficiency of OFA-2

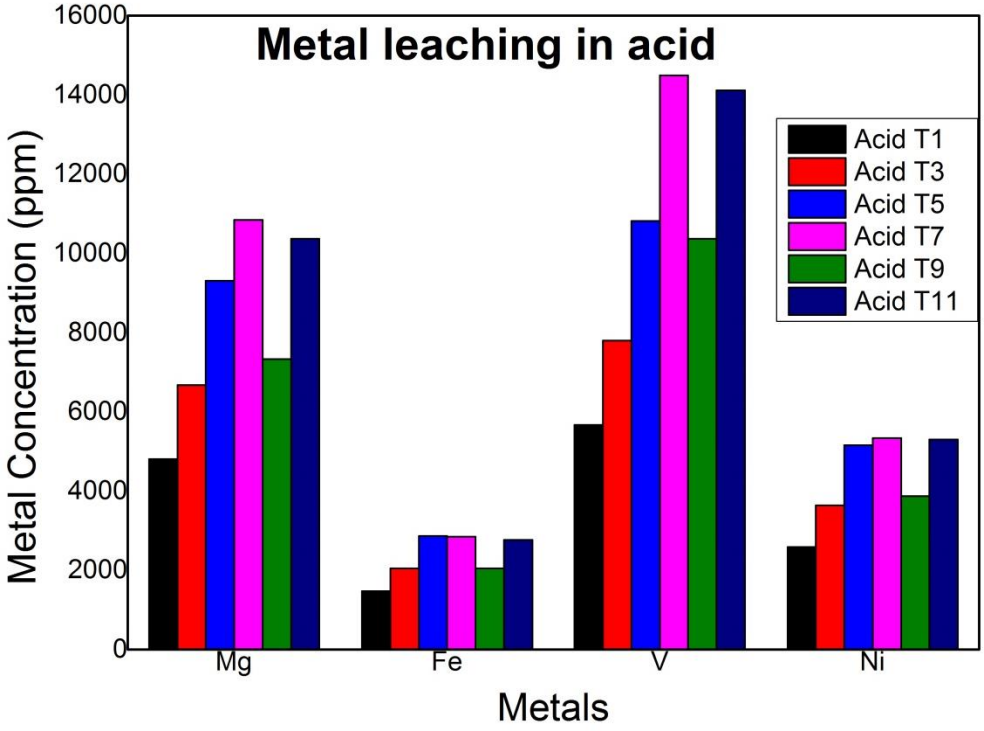


Figure 3-7 Metal leachability of water and acid of OFA-2

3.2.3 Alkaline treatment

Sodium hydroxide (NaOH) and ammonium hydroxide ($NH_3 \cdot H_2O$) were also used to leach metals from OFA. OFA samples were mixed with 100 ml 1N NaOH in a stainless-steel beaker and placed on a heating plate at 80˚C for one hour. The solution was then filtered and OFA samples washed by 500 ml deionized water. Ammonia treatment was conducted by refluxing concentrated $NH_3 \cdot H_2O$ at 100˚C overnight. The $NH_3 \cdot H_2O$ to solid ratio was 10: 1 (v: w = 10 ml : 1 g).

3.2.4 Water treatment

Due to the acidic property, OFA samples were washed by 100 ml deionized water, filtered, and dried in a conventional oven overnight. The water solution was recycled for washing fresh samples. It was recycled five times, and each time after filtration the volume was recorded and fresh water added to make up the total volume to 100 ml.

3.3 Activation

Physical activation was applied to activate recovered carbon. Ten grams of carbon was weighed and placed in a quartz tube of a Lindburg Blue M horizontal furnace. After the system was set up, the sample was first purged by N_2 for five minutes to remove the air in the tube, then the furnace temperature was programmed from room temperature to 900˚C at 10˚C per minute increments. The N_2 was passed through the tube for one hour to ensure pyrolysis to decompose the organic matter in the sample, then switched to CO_2 for another hour to develop pore structure and to burn off carbon. Then the tube was cooled to room temperature and the carbon weighed. The burn-off can be calculated as:

Burn off %= $\frac{w_{raw}-w_{AC}}{w_{raw}} \times 100\%$

Where,

w_{raw} is the weight (g) of dried raw fly ash added to the tube

w_{AC} is the weight (g) of AC

3.4 Result and Discussion

3.4.1 BET surface area

The BET surface area is an important index of physical adsorption: the higher the surface area, the better physical adsorption capability the AC has. The BET surface area results are listed in Table *3-1*. Ammonia hydroxide ($NH_3 \bullet H_2O$) and sodium hydroxide (NaOH) (record as AC-Ammonia and AC-NaOH) were utilized as chemical activation reagents. The results show that the surface area of AC-Ammonia slightly improved than the raw FA: from 2 m^2/g to 13 m^2/g. Similarly, the NaOH-aided physical activation did not improve the surface area, but morphological differences can be detected by SEM analysis (Figure *2-4* toFigure *2-8*). AC-OFA activated by physical activation and ammonia treated chemical activated FA show similar surface area after activation, while the meso and macro pore volume of AC-OFA is larger than AC-Ammonia. Compare with raw FA, physical activation can eventually improve the surface area by 10 times, and chemical activation improved it by 7 times. Density Functional Theory (DFT) method is selected to analyze pore size distribution in micro and meso pore size ranges. A general method to analyze mesopore distribution is BJH desorption, however; it is difficult to analyze micropore and narrow mesopore structure (Quantachrome-Instruments, 2010). The model condition was set to analyze PSD for N_2

adsorption, and the geometry was set to slit. After activation, ammonia treated FA can also improve the surface area, however it is not as good as physical activation. Adsorption linear plots are shown in Figure 3-8 and Figure 3-9. Pore size distributions by DFT model are shown in Figure 3-10 and Figure 3-11.

Table 3-1 BET results of different FA

Sample	Temperature (˚C)	Pyrolysis time (hour)	CO_2 Contact time (hour)	BET (m^2/g)	Micro Pore (cm^3/g)	Meso and Macro Pore (cm^3/g)	Pore Width (nm)
AC-OFA	900	1	1	20.7799	NA	0.042	10.8920
AC-Ammonia	900	1	1	15.5201	NA	0.024	10.7359
FA-Powder	900	1	1	13.1210	NA	0.030	7.6364
FA-Raw	-	-	-	2	NA	NA	NA

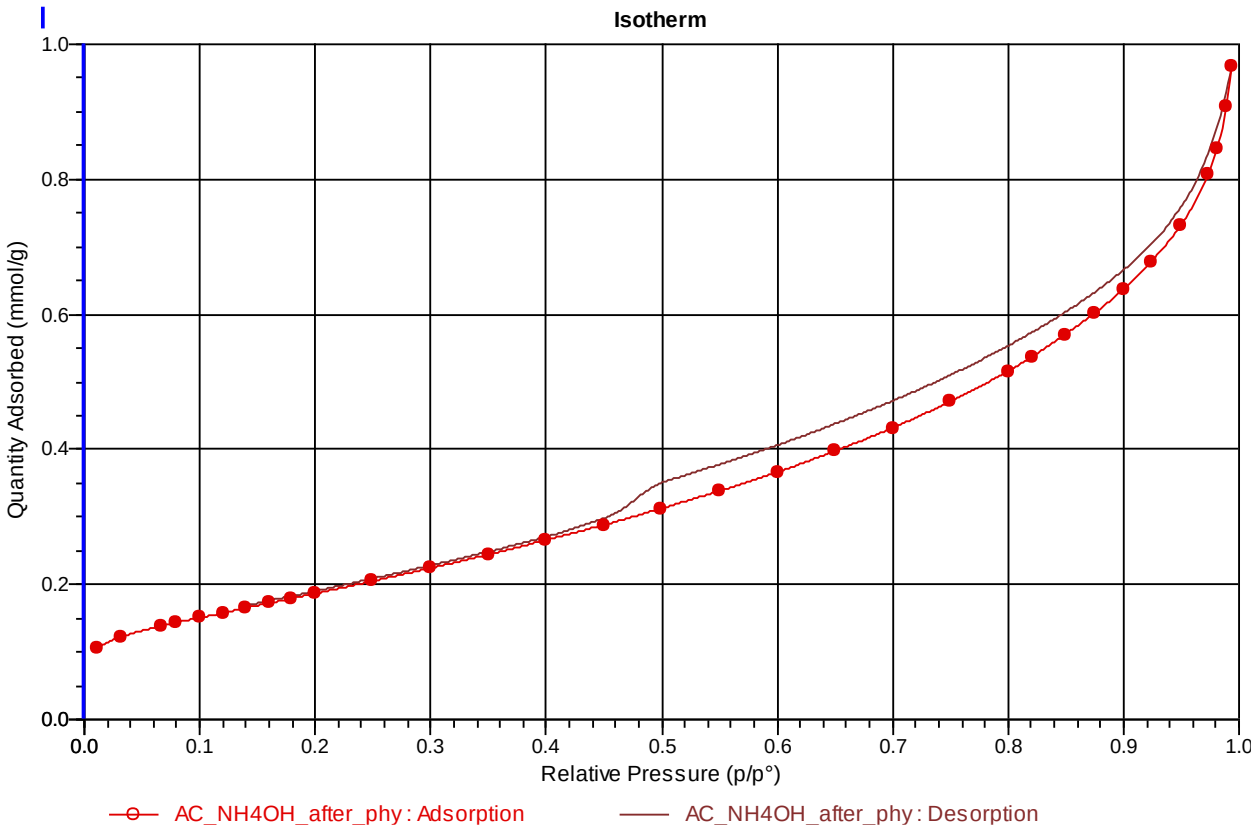


Figure 3-8 Isotherm linear plot of AC-Ammonia

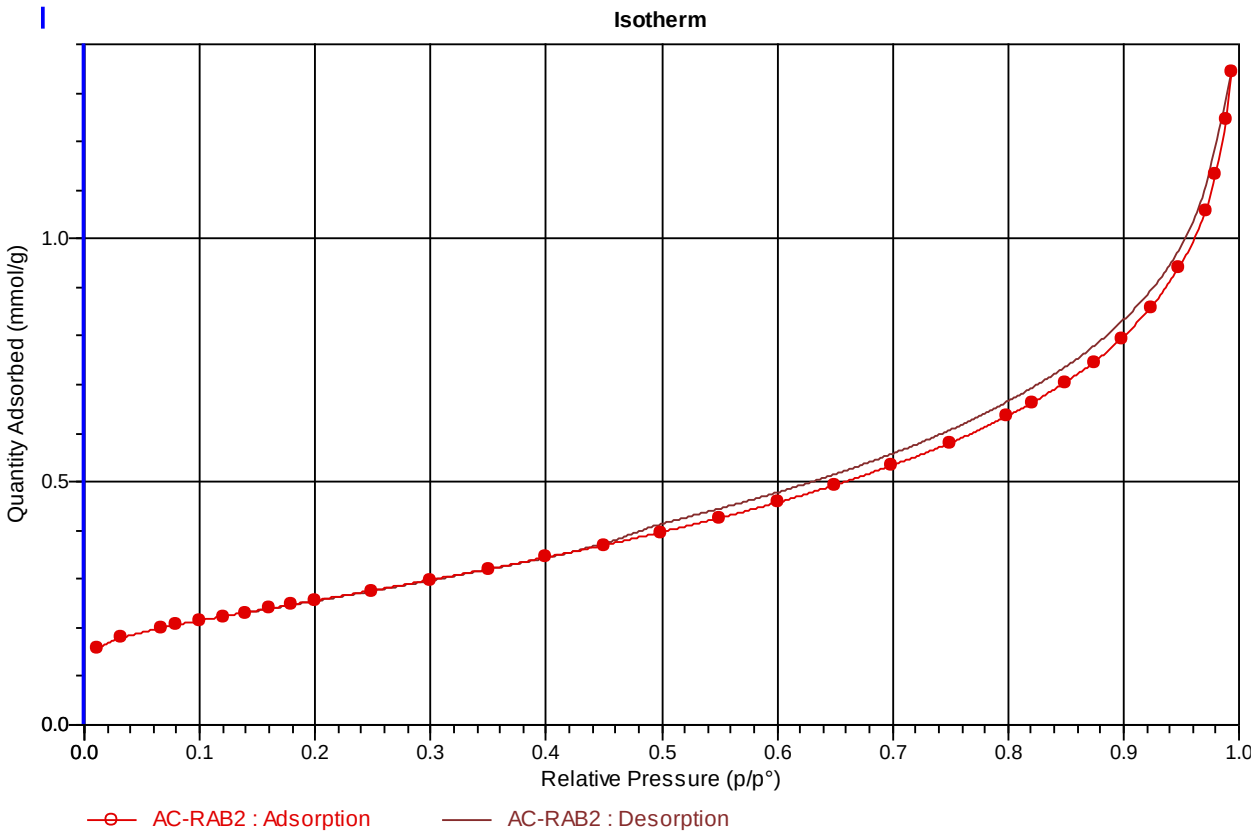


Figure 3-9 Isotherm linear plot of AC-OFA

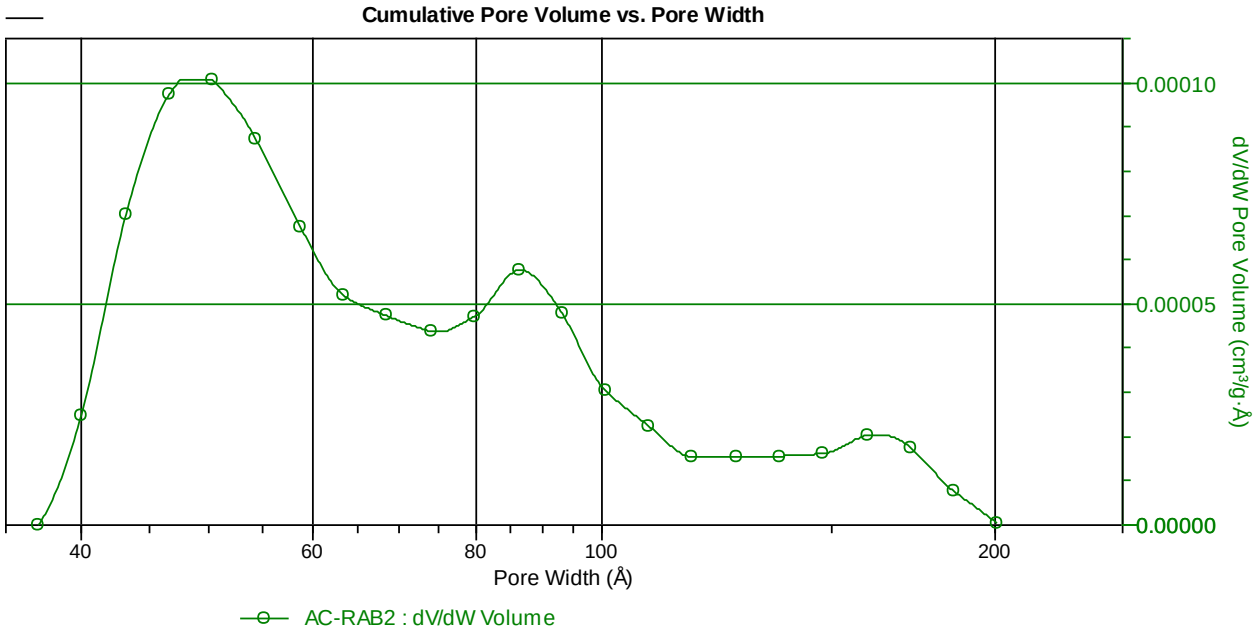


Figure 3-10 Pore size distribution of AC-OFA

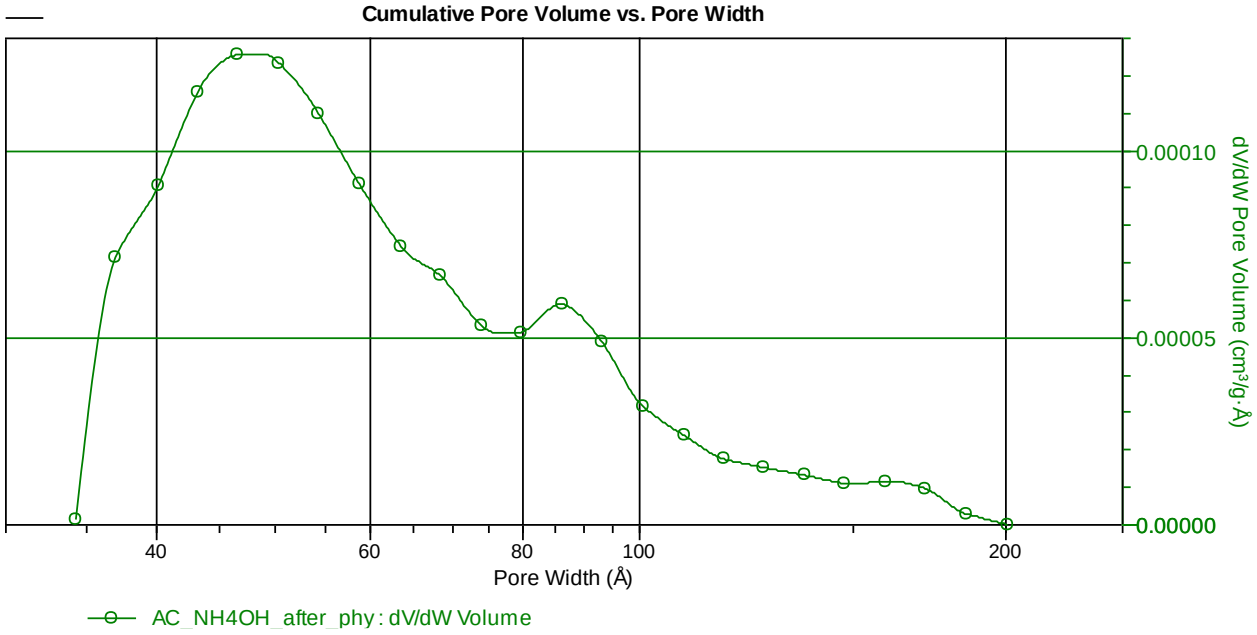


Figure 3-11 Pore size distribution of AC-Ammonia

All linear isotherm plots illustrated type IV adsorption curve and H4 hysteresis loop. The adsorbent showed no limit of adsorption at a relative pressure of 1, which could due to the slit pore or internal pore network structure. Adsorption and desorption loop closed at relative pressure of 0.46, Almost vertical of the adsorption curve at high relative pressure area indicates the wide macro pore width. Adsorption before relative pressure of 0.35 belongs to monolayer adsorption; after that, multilayer adsorption occurs. All OFA samples showed linearity adsorption before a relative pressure of 0.8, single point BET surface area can be calculated by picking the point around relative pressure of 0.3.

Broad pore size distribution can be divided into three relative pressure intervals: 0-0.01 is primary micropore interval; 0.01-0.4 is secondary micropore interval and 0.4-0.95 is mesopore interval (Bjelopavlic, 1999). Pore size distribution of OFA-Ammonia is shown in Figure 3-11, the sample has a wide meso-pore distribution ranged from 2.5 nm to 42.5 nm, while AC-OFA has a wider distribution from 2.5 nm to 73 nm. Both samples show no micropore distribution and broad distribution of mesopores. This also matches the negative micropore surface area in BET surface area result. The majority pore distribution ranges from 3.8 to 20 nm. Both samples are non-micropore and mesopore dominated carbon.

Chapter 4. Application of Fly Ash as Adsorbent in Water Treatment

4.1 Background

4.1.1 Current drinking-water-quality status in Newfoundland and Labrador

Microorganisms and chemicals in drinking water are difficult to remove through conventional water-treatment methods. To eradicate microorganisms, chlorine is commonly used as an effective disinfectant. In the presence of NOM in the water (USEPA, 2009), the residual chlorine reacts with dissolved organic carbon (DOC) and forms DBPs in the drinking water; these DPBs are now recognized as being potentially hazardous to human health under long-term exposure scenarios. Therefore, more attention in recent years has been on how to reduce DBPs in the drinking water in those communities where a complete treatment system, using advanced treatment technologies, is cost-prohibitive.

In Canada, most water-treatment plants use chlorine for both primary and secondary disinfection purposes. The evaluation results of the 2001–2004 Drinking Water Surveillance Program (DWSP) showed that 165 of 179 (92%) treatment plants in Ontario use chlorine as their primary disinfectant. In the province of Newfoundland and Labrador (NL), over 90% of the treatment plants use chlorine as the primary disinfectant. Although the provincial government has taken actions to improve drinking-water quality with measures such as source-water protection and operators' education (e.g., the source-to-tap program (DOEC, 2001)), communities still have DBP concentrations exceeding the drinking-water-quality guidelines.

NOM, as a precursor that causes the formation of DBPs in drinking-water systems, is commonly measured as total organic carbon (TOC). It is added to natural water bodies by natural processes such as soil chemical reactions, hydrological processes, organic materials, and a complex mixture of aromatic and aliphatic hydrocarbons (Leenheer and Croué, 2003). In general, NOM can be classified into two groups: the first is dominated by humic substances, which are hydrophobic in character and contain mostly humic and fulvic acids; the second consists mainly of non-humic substances and is a combination of organic compounds such as hydrophilic acids, proteins, amino acids, and carbohydrates.

As the reaction between NOM and residual chlorine can cause the formation of more than 600 forms of DBPs in a water-supply system, it is difficult to monitor all of them. Recent literature has focused on two groups, trihalomethanes (THMs) and haloacetic acids (HAAs), which form the largest class of DBPs in chlorinated drinking-water systems. Chloroform ($CHC1_3$), bromodichloromethane (BDCM) or $CHBrCl_2$, chlorodibromomethane (CDBM) or CHB_2Cl, and bromoform ($CHBr_3$) are compounds within the THM group. The sum of their concentrations, known as total trihalomethane (TTHM), should not exceed 100 µg/L (Health-Canada, 2012). There are nine compounds within the HAA group: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), and tribromoacetic acid (TBAA); and three mixed chloro- and bromo- acetic acids: bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and bromochloro acetic acid (BCAA). The total combined concentration of the five most prevalent HAAs (MCAA, DCAA, TCAA, MBAA, and DBAA), known as HAA_5, should not exceed 80 µg/L (Health-Canada, 2012). In NL, especially in rural areas, the THM and HAA concentrations are much higher

than the Canadian drinking-water-quality guidelines of 100 μg/L and 80 μg/L, respectively (Health-Canada, 2012). Out of approximately 496 sampled public water-supply systems in the province, 122 displayed high levels of THMs, according to the Guidelines for Canadian Drinking Water Quality (GCDWQ) (DOEC, 2016b). Compared to the USEPA standard, however, approximately 159 out of 498 sampled public water-supply systems in NL display high levels of HAAs (DOEC, 2016a). This illustrates that approximately one-third of the public water supplies cannot provide safe, potable water. When this is considered in conjunction with the summer of 2016 drinking-water-quality index, it can be inferred that the majority of these exceedances occur in small, rural drinking-water systems, usually in combination with other parameter exceedances, particularly colour (DOEC, 2009).

As mentioned earlier, DBPs form mainly by the reaction between NOM and disinfectants like chlorine, but their formation is also affected by pH, water temperature, and seasonal variations (Ahmad, 2013). For instance, in winter their level is relatively lower than that in other seasons. This can also be understood in terms of lower temperatures, as microorganism activity in the source water is reduced, and, therefore, less organic matter exists in the water. Since a large percentage of NL communities generally use surface pond water as their drinking-water source, DBPs are monitored regularly by the Water Resources Management Division of the Department of Environment and Conservation (WRMD-DOEC).

Surface water, such as rivers, ponds, and lakes, is often surrounded by bushes and is exposed without any protection. When it rains, these ponds can be contaminated by sediments and organic matter in the soil; hence, the water in these rivers, ponds, and lakes is generally considered to contain more organic matter than groundwater. This organic matter is usually considered a major

source of DBPs (Kar, 2000). According to the 2013 annual report (DOEC, 2014) of the Government of NL's Department of Environment and Conservation (DOEC), NOM concentration in the province's drinking water was as high as 11 mg/L. Additionally, mostly water reaches the supply system through distribution pipes, is stored in water supply tanks, and distributed to household units. It is important to estimate the duration that the water stays in these distribution pipes before it reaches consumers (Baribeau et al., 2004, Dion-Fortier et al., 2009). Research has shown an increase in THM concentration with time in storage tanks and pipe systems (Weinberg et al., 2006, Dion-Fortier et al., 2009). As the water remains in the pipelines in off hours, that is, midnight to morning, this allows extra reaction time between the free NOM and free residual chlorine, causing an increased concentration of DBPs in the water-supply system (Ahmad, 2013, Sadiq and Rodriguez, 2004).

4.1.2 Small community challenges in drinking-water treatment

The sparse geographical distribution of small communities in NL combined with community populations of generally fewer than 1,000 people does not lend itself to easy solutions to drinking-water-quality issues. These communities simply do not have access to the same resources (human or financial) as larger communities do. They have a lower median household income and fewer businesses and industry; this results in a lower tax base. Populations in most small communities in Newfoundland and Labrador are aging and declining in size. These factors make it more difficult for them to afford the infrastructure and qualified operators necessary to provide high-quality drinking water to their populations if water-quality issues arise (DOEC, 2009).

Small communities with very high THM and HAA levels in their drinking water do not have proper

water treatment in place and insufficient protection for their water sources. Water treatment facilities in these communities are equipped only with a pre-screen, such as a grate, to remove large pieces of matter, supplemented by a chlorine disinfection system, with no coagulation as pre-treatment or any kind of filtration for NOM removal. Pouch Cove does not have a water treatment plant and it relies solely on the chlorination of intake water and pH adjustments. Currently, chlorine disinfection is a preferred and economical choice for small communities like Pouch Cove.

4.1.3 Application of activated carbon for the removal of natural organic matter

The best available technologies to reduce NOM as identified by USEPA (2003) are enhanced coagulation and activated carbon (AC). The effectiveness of these methods, however, depends on pH, alkalinity, the dosage of coagulant and/or AC, and humic and non-humic NOM fractions in the water (Uyak and Toroz, 2006). Coagulation effectively removes humic substances and high molecular organic matter; carbon adsorption removes non-humic substances with low molecular weight, colour, and taste and odour-causing substances (Amy et al., 1992). AC, due to its high affinity to remove organic matter even at low concentrations, has been used in many water-treatment plants (Babi et al., 2007, Graese et al., 1987, Black et al., 1996). The Cincinnati Water Works, one of the world's largest granular activated carbon (GAC) filter systems for removing TOC, has an on-site GAC regeneration facility (Reinoso et al., 1997). A thermal reactivation study of spent GAC from this plant shows that the reactivated GAC has a comparable removal efficiency of TOC even after six cycles of use (Moore et al., 2001).

Although some of the commercially available AC, made from petroleum coke, bituminous and lignite coal, wood products, and coconut shells, show a high potential for removing DBPs and its

precursors, due to the high cost of the raw materials the AC manufactured from these materials is not economical and affordable in small communities (Streat et al., 1995). This has led to the need to find a low-cost adsorbent by extracting unburned carbon from OFA. This waste is abundant, with a huge amount being generated annually from the burning of heavy fuel oil (HFO) (Al-Malack et al., 2013). Only a small portion of OFA is reused for productive purposes; most is dumped into landfills (Shackelford, 2000). As reported in the literature, about 3 kilograms of ash residue is generated by burning 1000 liters of HFO (Tsai and Tsai, 1997); approximately 90% of this ash passes through the flue gas stream, which is collected by air pollution control devices such as ESP or cyclones (Hsieh and Tsai, 2003). On average, 50-60 tons of OFA is generated daily from a 2300 MW HFO-operated power plant (Steve and Turner, 2010, Hsieh and Tsai, 2003).

Millions of tons of OFA are generated yearly worldwide but very little is reused. The current practice, dumping OFA into landfills or waste containment facilities, causes potential environmental hazards (Fernandez et al., 2003, Mohapatra and Rao, 2001, Shackelford, 2000). Due to its low density (0.25 g/cm^3) and fine particulate size (average diameter 40-60 μm), OFA tends to travel long distances and can adversely impact plants, animals, and human health. Extracting carbon from OFA will not only minimize hazards but it will also significantly reduce its original volume.

Mofarrah et al. (2012) investigated the beneficial uses of OFA as a stabilizer or fill material by mixing it with cement (Mofarrah et al., 2012). Since OFA contains 70-85% unburned carbon, it has a high potential as an adsorbent. Recent studies show that OFA can remove phenols, methylene blue, lead, and chromium VI from wastewater streams by up to 92% (Mofarrah et al., 2014). OFA also has a high affinity for removing TOC from intake water sources in Pouch Cove and other

communities with high levels of THMs and HAAs in their drinking water supply systems (Husain and Ahmad, 2015).

The extracted carbon from OFA has shown promising results in reducing TOCs from the water-supply systems of two communities (i.e., Pouch Cove and Torbay) near St. John's (Ahmad, 2013). In the Pouch Cove system, the TOC level of 13.64 mg/l was reduced by more than 70% by the clean carbon. There was also a considerable improvement in turbidity reduction in the filtered water. Although these results are promising, they are based on only a few non-activated samples. Through an activation process, the surface area and pore size will be increased considerably. In this way, AC could be generated.

AC has been applied as a filtration material in water-supply systems for many years, effectively removing toxic chemicals, gases, and unwanted contaminants from water sources. The adsorption ability of AC varies with its porous structure. A good AC should have high porosity, increased surface area, suitable pore distribution, and high mechanical strength. In previous studies, AC has mostly been used to remove NOM, TOC, DOC, taste, odour, micro pollutants, and heavy metals (Kim, 2009).

4.2 DBP Precursor Removal

4.2.1 Water sample

In this study, water sample was collected from town of Pouch Cove. Pouch Cove is a town located 27 km north of St. John's. The population of the town is about 1866. The TOC level of source water is about 13 mg/L and THM and HAA levels are about 211.86 µg/L and 347.67 µg/L, respectively. The water treatment process of the town is simply pumping water from water supply,

then passing a grate to remove coarse particles, such as plastic, leaves, and branches. After this, water will further be pumped to the treatment plant, in which pH adjustment and chlorination disinfection are processed. Chlorine flow, free chlorine and pH are monitored on site. Then treated water is supplied to residents.

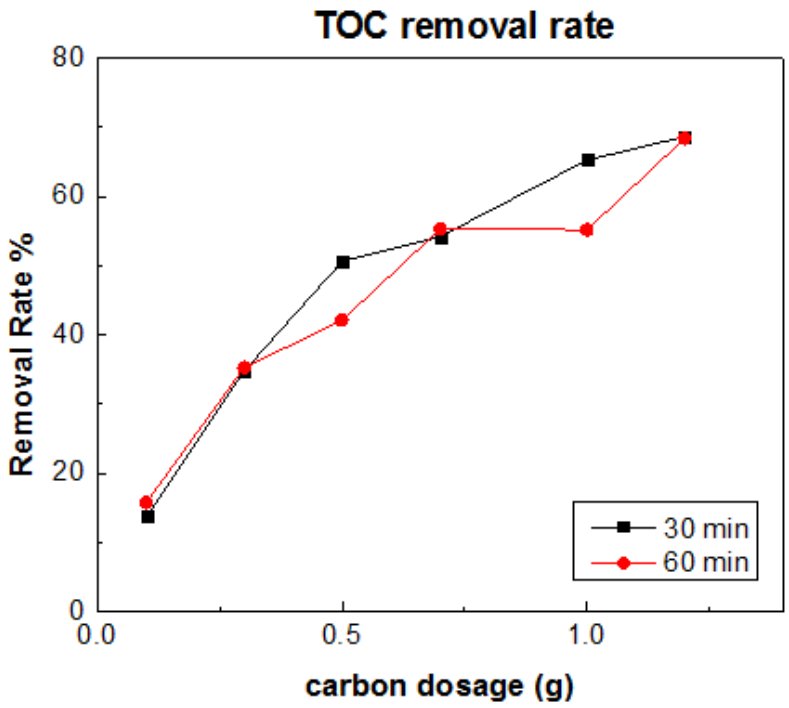
4.2.2 Batch test

A batch test was conducted to develop the relationship between the TOC removal rate and changes in UV_{254} values with parameters such as contact time and carbon dosage. For this, 100 ml of the water sample was added to a 250 ml conical flask; carbon dosages of 100, 300, 500, 700, 1000, 1200, and 1500 mg were added to the sample. The flasks were placed on a mechanical shaker at 120 rpm for 30, 60, 120, 240, 360, and 1440 minutes to mix the carbon and water. After shaking, all the samples were filtered by 0.45 µm filter paper to remove the fine particles. The filtered samples were analyzed by a TOC analyzer and UV-Vis (HP 8452 UV-Vis analyzer). The results of these tests are listed in Table 4-1. To study the removal efficiency of TOC and UV_{254} with the contact times, these values were plotted against carbon dosages, as shown in Figure 4-1. The TOC removal plots show that the removal rate with a carbon dosage of OFA-2 from 100 mg to 1200 mg and 30- and 60-minute contact times has an increasing tendency; at a 1500 mg dosage point, an inflection point appeared, and both the 30- and 60-minute adsorption rates are lower than that for the 1200 mg dosage. When 1200 mg of OFA-2 AC was added to raw water, it achieved maximum absorbance within 30 minutes. When 100 mg of OFA-2 AC was mixed with raw water, the UV_{254} adsorption rate from 30 minutes to 24 hours ranged from 0.22 to 0.24, which indicates that 100 mg of OFA-2 AC can reach saturation within 30 minutes. No matter how long it mixed with the water, no more organic matter could be removed. Similar to UV adsorption, the TOC removal rate

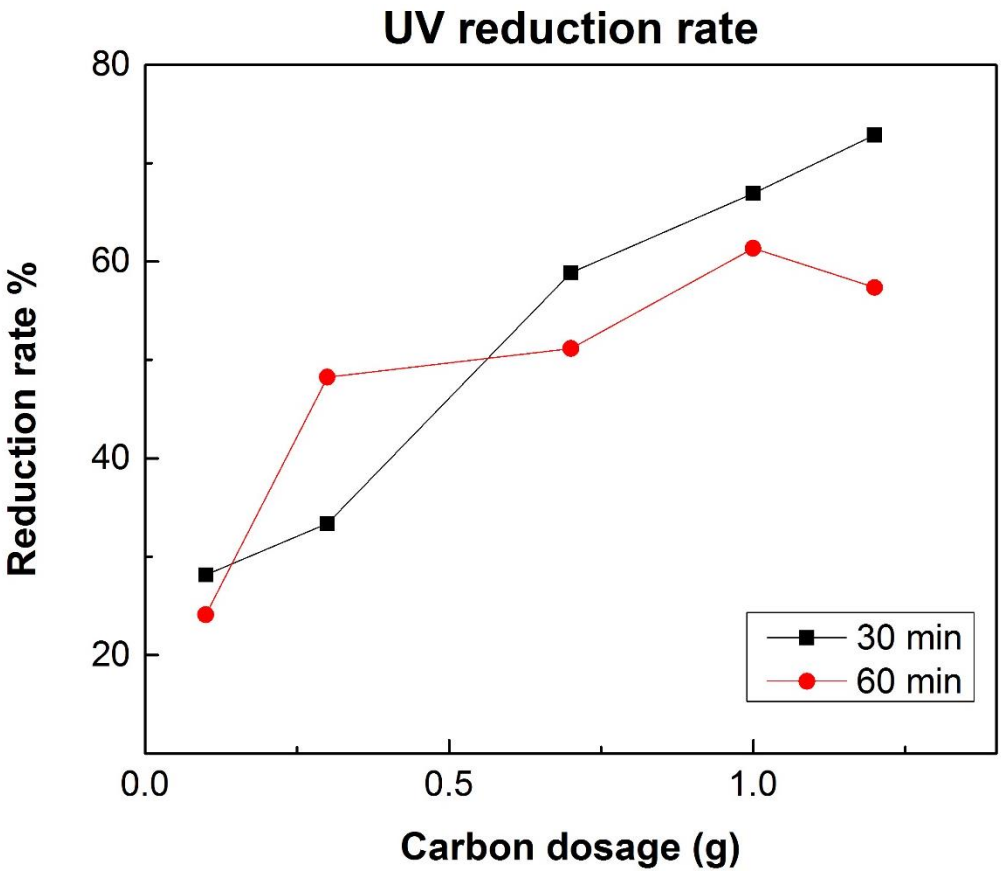
using 100 mg of OFA-2 AC for different contact times ranged from 13.66% to 18.86%. The dosage of 300 mg of OFA-2 AC showed the highest, 40% removal of TOC at 120 minutes and 52% removal of UV_{254} at the same time. Figure *4-1* and **Error! Reference source not found.** shows that the highest TOC removal rate was achieved at a 30-minute contact time by using 1200 mg of OFA-2 AC.

Table 4-1 Results of batch test

Carbon dosage (mg)	Contact time											
	Minutes											
	30		60		120		240		360		1440	
	UV_{254}	TOC	UV_{254}	TOC	UV_{254}	TOC	UV_{254}	TOC	UV_{254}	TOC	UV_{254}	TOC
0	0.32	8.895										
100	0.23	7.68	0.24	7.497	0.22	7.217	0.24	7.443	0.22	7.463	0.22	7.621
300	0.21	5.803	0.17	5.76	0.15	5.352						
500	0.14	4.394	0.27	5.152								
700	0.13	4.076	0.16	3.977								
1000	0.11	3.092	0.12	3.988								
1200	0.087	2.788	0.14	2.811								
1500	0.017	3.066	0.22	2.933								


TOC removal rate
Removal Rate %
carbon dosage (g)
0
20
40
60
80
0.0
0.5
1.0
30 min
60 min

(a)



(b)

Figure 4-1 TOC and UV removal by carbon dosage

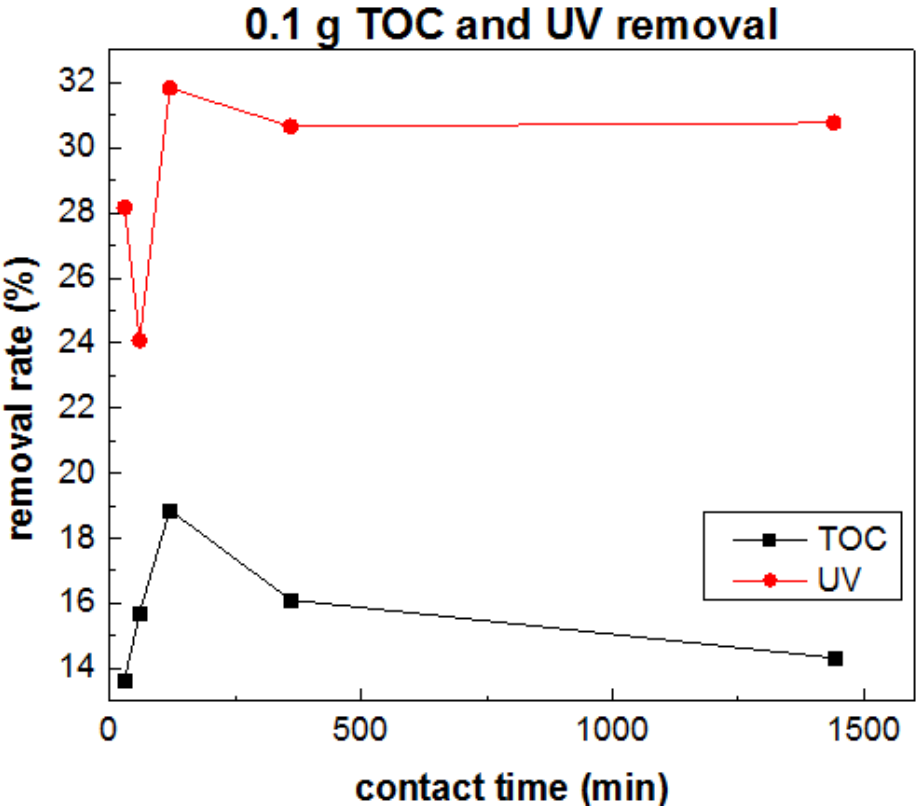


Figure 4-2 Toc removal and UV reduction by time

4.3 DBP Formation Potential

After filtration by activated carbon, water sample collected from community was disinfected by sodium hypochlorite (NaClO) to find the formation potential of DBP. To find the formation potential, contact time was one hour and the free chlorine concentrations after disinfection were controlled from 0.1 mg/L to 2 mg/L. Then HAAs and THMs generated during disinfection process were analyzed by liquid-liquid extraction and followed by a GC (HP-6890) coupled with a μ-ECD detector (EPA, 1995b, EPA, 1995a). The results are shown in Figure 4-3 and Figure 4-4. As shown in this table, with the same amount of TOC different concentrations of chlorine significantly affect THM formation. One hundred milligrams of AC-OFA mixed with raw water and chlorinated at different chlorine doses (0.1 mg/L to 2 mg/L). The TTHM concentration of the less chlorinated sample was only one-third that of the high-level chlorination. The results show that, after chlorination, raw water had the highest TTHMs and THAAs. Compared with the tap water collected from Pouch Cove, both concentrations are very close. Variation may be due to seasonal change and different collection times (Ahmad, 2013). A comparative assessment was conducted with different levels of free chlorine added to the filtered water, as shown in Figure 4-3 andWhere:

Filtered water: water chlorinated by NaClO after filtration by AC-OFA;

Raw water: water sample directly chlorinated by NaClO without any treatment;

Tap water: water sample collected from Pouch Cove residents.

Figure 4-4. The formation of chloroform, generally considered the main compound in the THM group, is significantly affected by chlorine. Figure *4-3*compared raw water directly chlorination, with tap water collected from the site and supply water after filtration by AC-OFA. The results indicated that THMs are more easily to form due to the residue of free chlorine. The HAA formation potential is shown in Figure 4-4 indicates that after filtration by AC-OFA, the HAA formation can be eventually controlled.

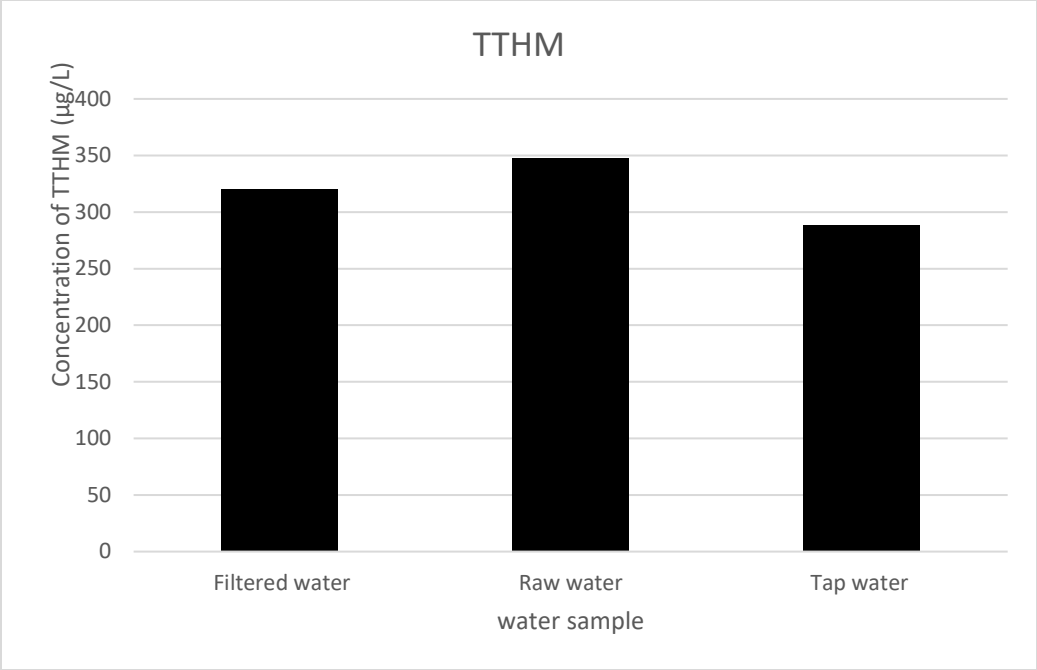


Figure 4-3 THM formation potential

Where:

Filtered water: water chlorinated by NaClO after filtration by AC-OFA;

Raw water: water sample directly chlorinated by NaClO without any treatment;

Tap water: water sample collected from Pouch Cove residents.

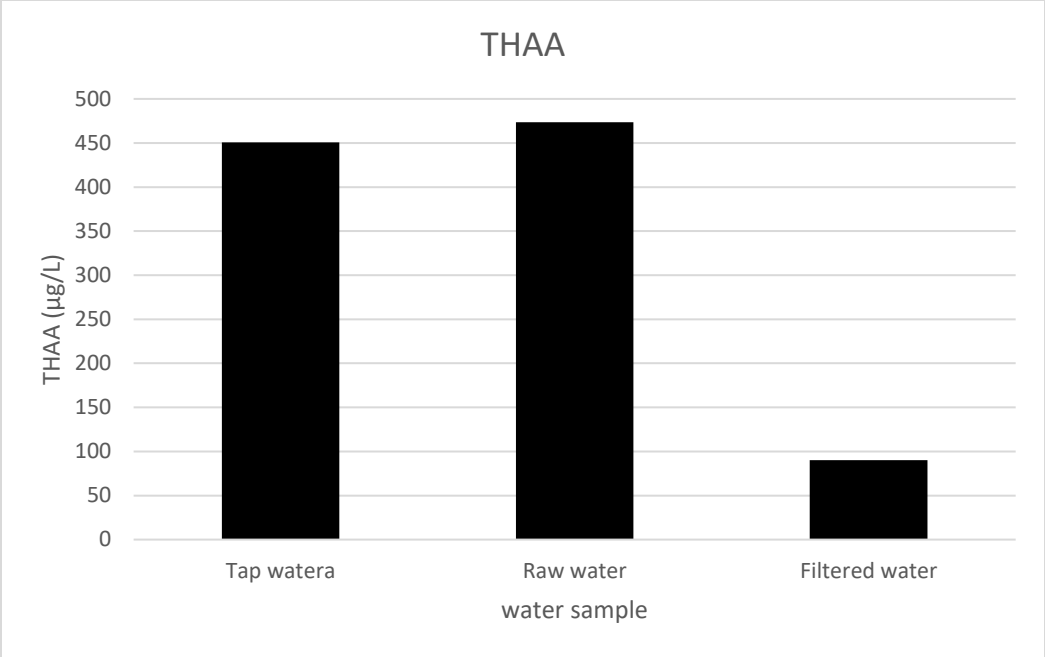


Figure 4-4 THAA formation potential

4.4 Optimization of TOC Adsorption Conditions

4.4.1 Design of Experiment

A widespread principal of experiment design is to change only one factor and keep all other factors stable at one time: one factor at a time (OFAT) approach. However, using this technique is very time consuming and cost intensive, especially for projects with a limited budget and urgent deadlines. Small projects with only two or three factors might be adapted by using OFAT, while experimenters can only find main effects and no effects as one depends on the others (Montgomery, 1991), and thus be selected in this study. Initially, a Center Composited Design was considered as the technique of choice for the experiment, which would bring in five levels of temperature. Limited equipment capacity and operating conditions make temperature control an obstacle to the operation. Split-plot design, therefore, was chosen to compromise the hard-to-change effect problem. This design is especially for experiments with hard-to-change factors, such as temperature, pressure, and water depth. With the application of a split-plot design, experiments can easily be split into several groups, each group containing one or more hard-to-change factors fixed at one level and randomized easy-to-change factors. The advantage of this design is that experiments can be conducted without changing the hard-to-change factors all the time; therefore, time is saved rather than waiting for these hard-to-change factors to reach designed conditions. However, the disadvantage of this design is that hard-to-change factors were grouped without randomization, whereas easy-to-change factors were randomized several times (Lye, 2014). For this reason, hard-to-change factors are usually difficult to analyze. More replicates are necessary to reach the desired 80% power of hard-to-change factors. Design Expert 9.0 software was utilized to determine the optimized condition of DBP precursor removal.

4.4.2 Determination of Factor Levels

Through a literature review, five main effects including pH (A), temperature (B), carbon dosage (C), sample volume (D), and contact time (E) were selected in this study. Several runs of pre-tests were performed to determine the range of factors. Since temperature is difficult to change, a two-level factorial split-plot design was chosen as the technique to model the experiment. Temperature is the hard-to-change factor with two replicates. The design of the experiment is listed in Table 4-2.

Table 4-2 Factors and levels of the experiment

Factors	Unit	Low level in actual value	High level in actual level
A: pH		2	8
B: Temperature	°C	25	35
C: Carbon dosage	mg	50	100
D: Sample volume	ml	50	100
E: Contact time	Hrs	0.5	4

4.4.3 Material and method

A water sample collected from the pond used as the source water for residents of the community of Pouch Cove, NL, was immediately transported to the laboratory and refrigerated at 4°C. Then 1N HCl and 1N NaOH were prepared from concentrated HCl and NaOH (Sigma Aldrich, Canada) for pH adjustment. Modified FA was prepared by acid washing and physical activation at 800°C of the FA collected from the local power plant. Samples were dried for 24 hours before use. A mechanical shaker was used for experiments at 25°C, while a heating plate with a magnetic stirrer

was used to heat the sample to 35°C and stir it to adequately mix it with the absorbent. UV_{254} was analyzed by HP UV-Vis 8453 at 254nm. UV_{254} of raw water sample is UVA=0.365 cm^{-1}.

Modified FA samples were mixed with the water sample in Erlenmeyer flasks at designated values. Mixed samples were reacted at different temperature and contact times to determine the removal rate. The heating plate was adjusted to a range of 35-40°C to keep the sample temperature around 35°C and a shaker was used to represent room temperature conditions. Treated samples passed through a 0.45 μm vacuum filtration to remove any visible particles and live microorganisms before UV and TOC analysis. UV_{254} was determined by a wavelength of 254 nm with a pathway of 1 cm, with MilliQ Ultrapure water as a blank.

4.4.4 Result and discussion

Table 4-3 lists the results at different conditions. The analysis indicates that the carbon dosage, water volume, and pH are the significant factors. As the block effect reduces the significance of temperature, the model cannot provide this significance and experiments are required to find the significance of temperature. Analysis of variance (ANOVA) results of TOC and UV are listed in Table 4-4 and Table 4-5 respectively. When the Probe>F value is smaller than 0.05, the model or the effect is significant, in this study the Prob>F value of both UV and TOC are < 0.0001, both models are significant. Analysis shows that carbon dosage, water volume and pH are significant factors of UV adsorption. Temperature, carbon dosage, pH, interaction between temperature and pH, water volume and pH are significant factors of TOC adsorption, in which water volume is not significant effect, it is chosen because the interaction effect between water volume and pH is significant. The Pred R-Squared of TOC of 0.9109 is in reasonable agreement with the Adj R-Squared of 0.9373. The Adeq Precision of 23.382 indicates an adequate signal. The Pred R-Squared of UV of 0.9445 is in reasonable agreement with the Adj R-Squared of 0.9561. Adeq Precision of UV of 34.215 indicates an adequate signal. For TOC, carbon dose and the interaction between water volume and pH have negative effects, while others all have positive effects. For UV, carbon dosage is the only factor has negative effect, and others all have positive effects.

Surface charge of activated carbon and the charge of NOM can be important factors in NOM adsorption process (Bjelopavlic, 1999). Small molecular weight NOM will have negative charge when the pH value is higher than 4. Meanwhile, if activated carbon also has negative surface charge, it will repel NOM, thus reduce the adsorption capability. FTIR results of OFA treated by different agents shown in Figure 2-9 indicate that most OFA contain oxyen contained groups

(mainly hydroxyl and carboxyl groups) on carbon surface. When increase the pH, these groups will cause the net charge increasingly negative, this explains the reduced adsorption of TOC and UV under alkaline condition. Other factors will affect adsorption are pore structure, surface area, surface impurities and etc. Figure 3-10 and Figure 3-11 show mesopore dominates pore size distribution. SUVA is also an important factor to identify hydrophobic or hydrophilic of NOM. In this study, the SUVA is about 3 which means the characteristic of NOM is hydrophilic dominated (Sillanpää, 2015). This kind of NOM is difficult to be removed by conventional coagulation (Sillanpää, 2015). Figure 2-9 shows AC-OFA sample utilized in this study is also hydrophobic due to non polar bonds after activation. The nature of the AC will also reduce the adsorption capability.

Another OFAT experiment specifically examined the effect of temperature during the procedure.

Table *4-6* indicates that raising the temperature significantly reduces the absorbance efficiency.

Table 4-3 Results of the experiment

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Response 1	Response 2
Run	A: Temperature	B: Carbon	C: Water	D: pH	E: Time	UV	TOC
	degree	mg	mL		hour	cm^{-1}	ppm
1	35	100	100	8	4	0.336	10.1
2	35	100	50	8	0.5	0.256	10.4
3	35	50	100	2	4	0.139	5.412
4	35	50	50	8	4	0.32	10.96
5	35	50	100	8	0.5	0.411	11.2
6	35	50	50	2	0.5	0.121	5.054
7	35	100	50	2	4	0.07	3.824
8	35	100	100	2	0.5	0.164	5.355
9	35	100	50	2	4	0.07	3.602
10	35	50	100	8	0.5	0.352	12.34
11	35	100	50	8	0.5	0.29	12.33
12	35	100	100	2	0.5	0.137	5.348
13	35	100	100	8	4	0.302	11.44
14	35	50	50	2	0.5	0.127	5.032
15	35	50	100	2	4	0.189	7.357
16	35	50	50	8	4	0.3	12.95
17	25	50	50	2	4	0.116	5.852
18	25	100	50	8	4	0.259	8.23
19	25	50	100	8	4	0.366	10.36
20	25	50	50	8	0.5	0.355	9.81
21	25	100	50	2	0.5	0.06	3.532
22	25	100	100	2	4	0.122	6.19
23	25	50	100	2	0.5	0.134	6.455
24	25	100	100	8	0.5	0.341	9.7
25	25	100	100	8	0.5	0.312	9.69
26	25	100	50	8	4	0.221	11.79
27	25	100	50	2	0.5	0.031	3.522
28	25	50	50	2	4	0.087	5.305
29	25	50	100	2	0.5	0.153	7.015
30	25	50	50	8	0.5	0.296	9.8
31	25	100	100	2	4	0.118	6.064
32	25	50	100	8	4	0.322	9.91

Table 4-4 ANOVA of TOC removal

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob>F
Block	3.82	1	3.82		
Model	259.17	6	43.19	75.77	<0.0001
A-Temperature	7.37	1	7.37	12.93	0.0015
B-carbon dosage	5.86	1	5.86	10.28	0.0038
C-water volume	0.49	1	0.49	0.87	0.3616
D-pH	153.67	1	153.67	269.56	<0.0001
AD	7.39	1	7.39	12.97	0.0014
CD	7.03	1	7.03	12.34	0.0018
Residual	13.68	27	0.57		
Cor Total	276.67	31			

Table 4-5 ANOVA of UV removal

Source	Sum of Squares	df	Mean Square	F-Value	p-value Prob>F
Block	2.126E-3	1	2.126E-3		
Model	0.36	3	0.12	218.69	<0.0001
B-carbon dosage	0.015	1	0.015	27.68	<0.0001
C-water volume	0.026	1	0.026	47.85	<0.0001
D-pH	0.32	1	0.32	580.55	<0.0001
Residual	0.015	27	5.515E-4		
Cor Total	0.38	31			

Table 4-6 Effect of temperature

Temperature	pH	Carbon dosage	Water volume	Contact time	UV_{254}	TOC
°C		mg	ml	hour	cm^{-1}	mg/L
25	6.7	100	100	1	0.268	8.474
35	6.7	100	100	1	0.36	11

Final equation of UV and TOC

$$UV = 0.027562 - 8.73750\text{E} - 004 * \text{carbon dosage} + 1.14875\text{E} - 003 * \text{water volume} + 0.033344 * \text{pH} \quad \text{Equation (4-1)}$$

$$TOC = 4.36316 - 0.10097 * Temperature - 0.017119 * carbon\ dose + 0.046185 * water\ volume + 0.40431 * pH + 0.032044 * Temperature * pH - 6.25125E - 003 * water\ volume * pH \quad \text{Equation (4-2)}$$

4.4.5 Validation of model

The model was validated by using point prediction of Design Expert software. Four different conditions were chosen to validate the model. The actual results and predicted 95% Confidence Interval are shown in Table 4-7.

Table 4-7 Validation of the model

Temperature	Carbon dosage	Water volume	pH	Contact time	UV	Predicted
25	60	80	6.5	0.5	0.268	(0.239, 0.339)
30	70	55	4	1	0.135	(0.113, 0.223)
25	80	50	3	1	0.133	(0.073, 0.163)
30	90	60	7	2	0.255	(0.194, 0.304)

The results of the chosen conditions to validate the model indicate that the UV reduction is stable and can fall into predicted 95% confidence intervals. Most of the validation experiment results are very close to the mean of predicted points. This model is relatively accurate and can be applied in real experiment prediction. However, in real cases, adjusting the pH value to very low is not reasonable; adjusting carbon dosage and water volume to the optimized condition could achieve the highest UV_{254} and TOC absorbance.

Chapter 5. Oil Spill Cleanup Using Oil Fly Ash

5.1 Background

Offshore oil spills during drilling or transportation has been a major concern of marine contamination (Karakasi and Moutsatsou, 2010). The most frequently utilized technologies to treat offshore oil spills are boom and dispersants. However, with the application of dispersants, an oil film is dispersed into small droplets and dissolved in the ocean, and water and the toxic components remain in the water columns and sediments. The new trend with oil spill cleanup is to develop adsorbent and absorbent materials to remove both the floating and dissolved fractions with minimum environmental effects.

The low density of oil will form a floating oil layer on the ocean surface and spread a long distance by winds and waves; it will finally disperse over a large area, with the surface oil sheen causing devastating effects on seabirds and marine habitats (Ivshina et al., 2015).

In-situ burning, oil containment boom and skimmer are conventional methods used n in offshore oil spill clean up to directly ignite spilled oil on the site or physically collect oil and prevent spreading, while this requires huge amount of manpower and it highly depends on the environment (Ivshina et al., 2015). In-situ burning can cause serious impact on air quality. Organic synthesized material, such as polyurethane foam; mineral materials, such as silica based aerogel, and inorganic materials, such as carbon soot, zeolite show great potential in oil adsorption (Adebajo, 2003, Sayed and Zayed, 2006). Chemical dispersant, bioremediation have been widely used in oil spill response (Ivshina et al., 2015). Advanced technology is to hydrothermally treat FA or other materials,

followed by freeze drying and finally develop a 3-dimension hydrophobic carbon sponge. This type of sponge can generally adsorb up to hundreds gram of oil per gram carbon. However, the nature of these materials (including CFA) are hydrophilic, extra surface modification is required to change hydrophilic to hydrophobic (Karakasi and Moutsatsou, 2010, Sakthivel et al., 2013, Banerjee et al., 2006). However, due to high energy consumption, the economic feasibility remains a concern. It is therefore important to find an economically feasible high capacity oil adsorption material.

The sponge-like structure of OFA has the potential to be an excellent absorbent of large molecular floating oil. In this research, a batch test was conducted to simulate the treatment of an offshore/shoreline oil spill by acid treated OFA and AC-OFA.

5.2 Materials and Experiment

Crude oil from Newfoundland and Labrador offshore oil field was used for this study; seawater was collected from the St. John's shoreline; and acid treated OFA and AC-OFA were prepared and modified by the method discussed in chapter 3.3.

Oil absorption capability was tested by adding 0.4 grams of FA and AC to 100 ml seawater which was contaminated by 250, 500, 750, 1000 and 1250 μL crude oil and shaken for four days at 80 rpm to achieve full absorption.

A thermogravimetric analysis (TGA) method was applied to analyze the weight of oil absorbed by 1 gram of carbon material (Sakthivel et al., 2013). The flow was set at 50% of air balanced by 50% of N_2. The furnace temperature was programmed to increase from room temperature stepwise to 100°C by 20°C per minute increments. Then hold at 100°C for five minutes to remove water, and

the weight of water adsorbed can be found by calculating the weight difference. Continued increasing temperature at 20°C per minute increments to 500°C to determine the absorbed oil weight by calculating the weight difference between the two temperatures as shown in equation 5-1. The results are presented in Figure *5-1* to Figure *5-11* and Table *5-1*.

$$Oil\ adsorbed\ \left(\frac{g\ oil}{g\ OFA}\right) = \frac{m\times(W_{100-400}\%)}{m\times(1-W_{H2O}\%-W_{100-400}\%)} \quad (5\text{-}1)$$

Where:

m: the initial weight placed in the sample pan,

W_{H2O}%: weight change (%) before 100 ºC, the weight loss due to water evaporation and low molecular portion of oil,

$W_{100\text{-}400}$%: weight change (%) between 100 and 400 ºC, the weight loss due to burning adsorbed oil

5.2.1 Result and discussion

Figure 5-1 shows the TGA result of raw AC: the weight dropped significantly from 500°C, from room temperature to 500°C, the AC weight kept stable, which means no weight loss in the period. Same as derived weight change, it began to increase since 500°C, which matched weight change trend. Figure *5-2* toFigure *5-6* show the TGA of oil-adsorbed ACs; the first weight loss is found at 100°C, which is the evaporation of water and small molecular portion of oil adsorbed by AC. This is followed by a weight loss which occurred when the temperature increased from 100°C to 425°C, which was due to the burning of oil. During the temperature increase from 425°C to 500°C the weight change can be due to the weight loss of the combination of oil and carbon. Derived weight

changes also give the same trend: two sharp peaks occurred at 100℃ due to the loss of water—the first is the initial evaporation of water and low oil, and the second is the thorough removal of water and low oil during the five-minute retention time at 100℃. During the oil burning process, a trend of increasing weight change per Celsius from 100ºC to 200ºC, then being stable from 200ºC to 300ºC, and decreasing from 300ºC to 425ºC for all samples. The initial increasing is due to the beginning of burning oil, then the stable is due to the continuing burning of oil. During last period, the decreasing of weight change per Celsius is due to the end of burning oil and the temperature is still between the oil burning and OFA burning period. The increase of weight change per Celsius from 425ºC is due to the beginning of OFA burning. The TGA result of raw AC shows thermal stability from room temperature to 500℃ as the weight loss began from 460℃ to 500°C. Figure 5-7 to Figure 5-11 show the results of TGA after oil adsorption by FA. Two sharp peaks can be found at 100°C on the curve of derived weight change, this is due to the water and low molecular portion of oil evaporation at 100°C. Because of the fast temperature increasing speed, both water and low molecular portion of oil evaporated very fast, and formed the sharp peaks. The large amount of water adsorption occurred when only 0.25 ml and 0.5 ml of oil was added in the system. This may be due to the reason that the small portion of oil did not reach the capacity of OFA. A rising slope of the curve occurred between 100 and 425°C due to the burning of adsorbed oil. The sharp drop at 425°C shows the end of the oil burning. carbonization and carbon burning. The oil absorbed by weight can be found in Table 5-1.

Table 5-1 shows the oil adsorption capacity of AC and FA. Overall, the average capability of oil adsorption of both acid treated OFA and AC-OFA are about 1 $\frac{g\ oil}{g\ OFA}$. The overall adsorption

performance of acid treated OFA was slightly better than the performance of AC. The adsorbed oil per gram of carbon comes close when increasing the concentration of oil in water. After four days of adsorption, both AC and FA can keep floating on the seawater surface and no powder is found on the bottom of the flask. The contact angle of AC-OFA and acid treated FA are both about 110º. This indicates that OFA is hydrophobic. Regarding oil cleanup adsorbent, research has been conducted mostly focusing on modifying CFA to high surface area and converting it into hydrophobic zeolite powder. Due to high concentration of SiO_2 content in CFA and the polar nature of -Si-O- bond, CFA is a hydrophilic and low carbon content material. To reach high surface area and hydrophobic characteristics, it requires various chemical treatment process, which are not required for OFA. For powder material, the final adsorption capacity of treated CFA and OFA are almost the same. OFA can therefore be a good candidate as a potential oil spill cleanup material.

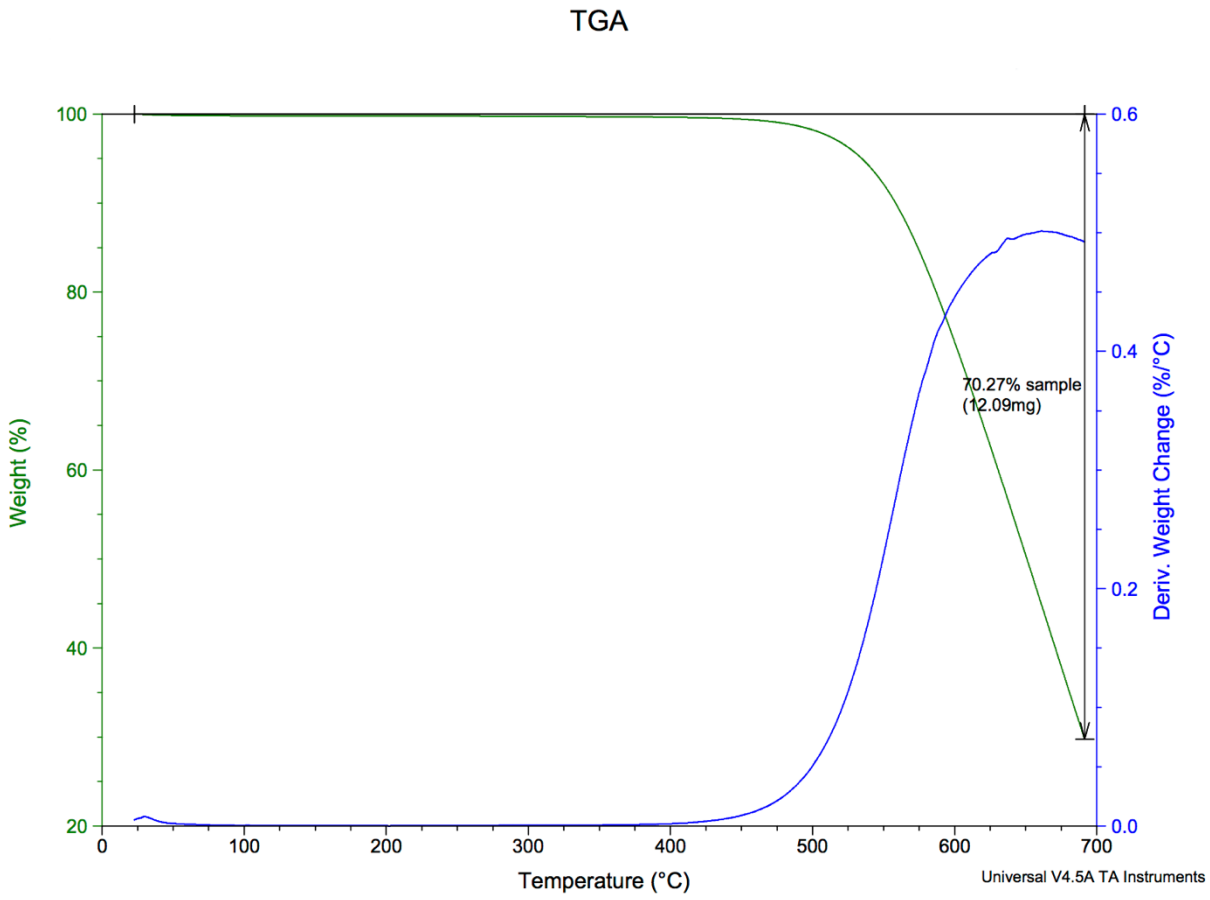


Figure 5-1 TGA of raw AC

Where:

Weight (%): the weight percentage of FA left during the temperature increasing period;

Deriv. weight change (%/°C): weight change by per Celsius temperature increasing

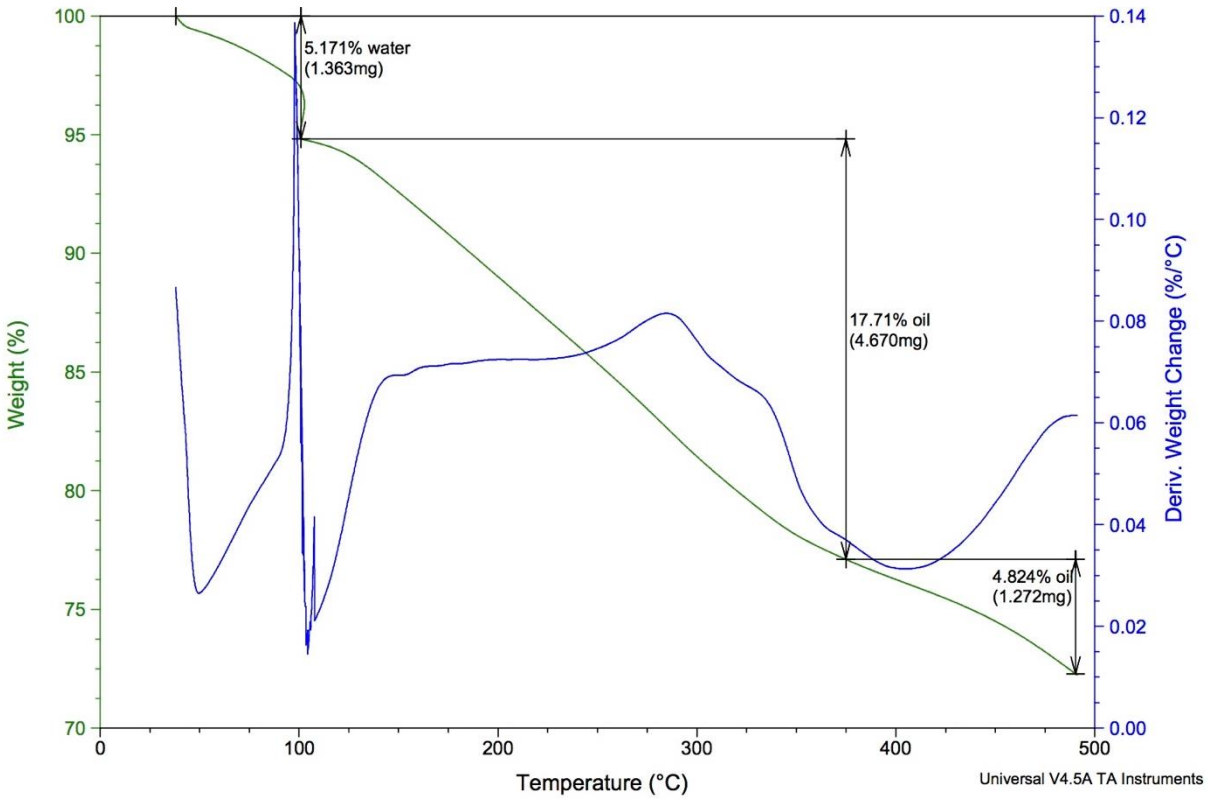


Figure 5-2 TGA of 0.25 ml oil AC

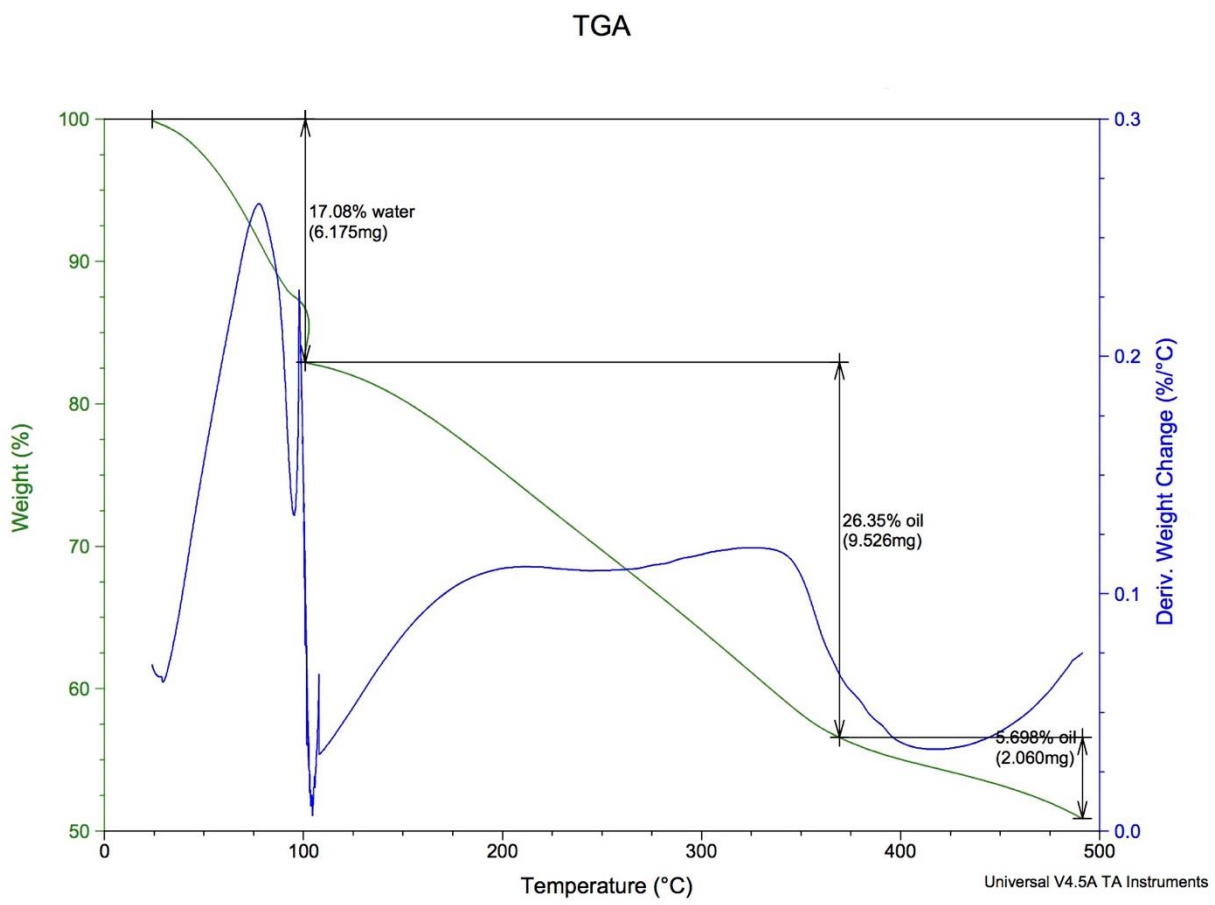


Figure 5-3 TGA of 0.5 ml oil AC

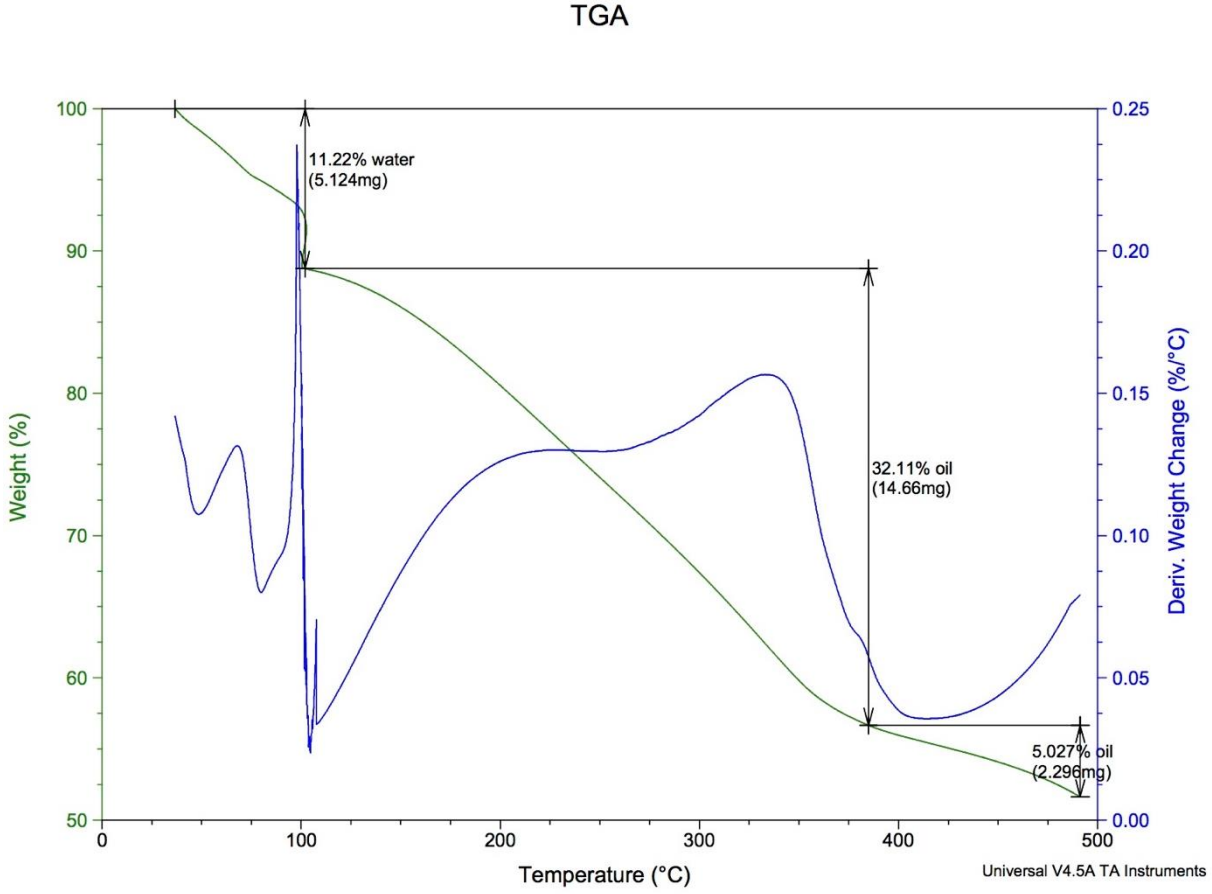


Figure 5-4 TGA of 0.75 ml oil AC

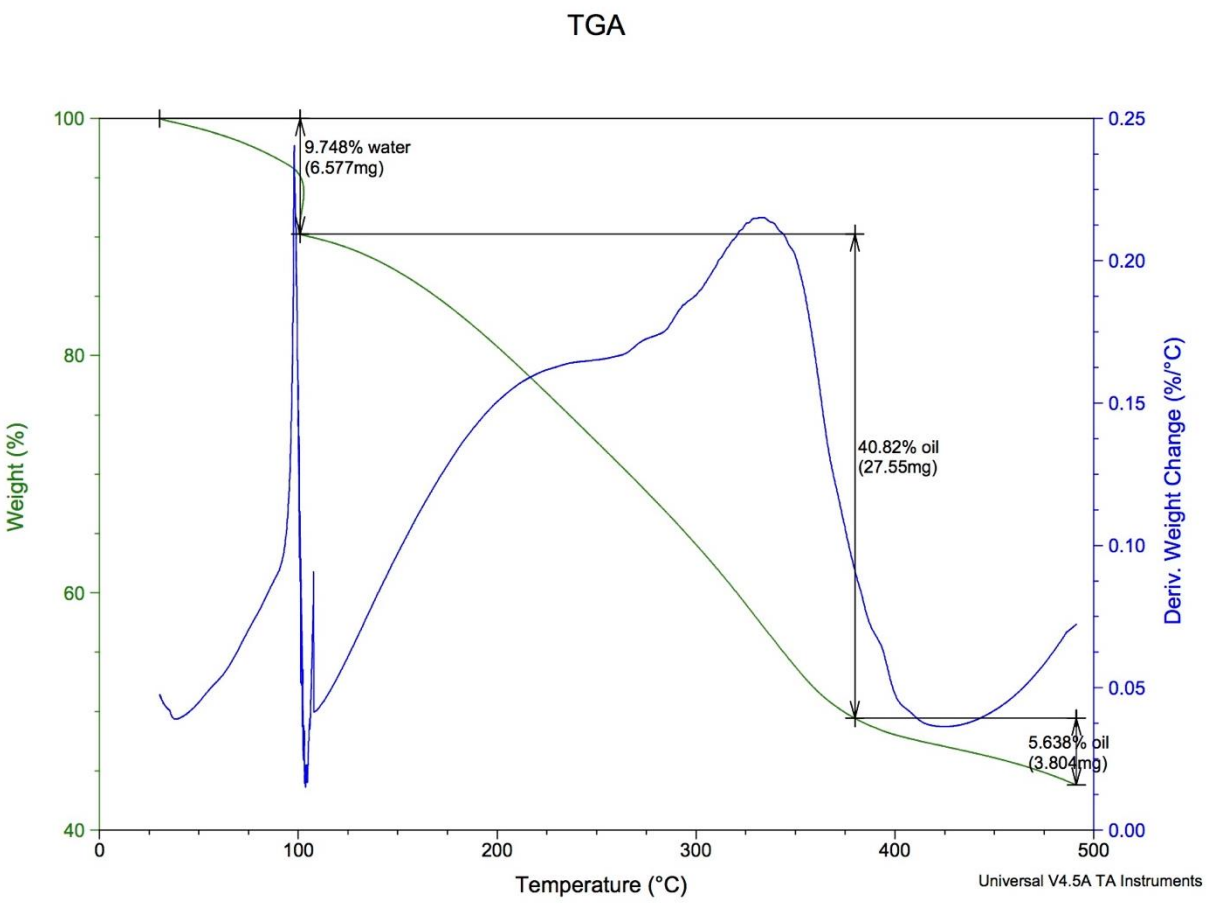


Figure 5-5 TGA of 1 ml oil AC

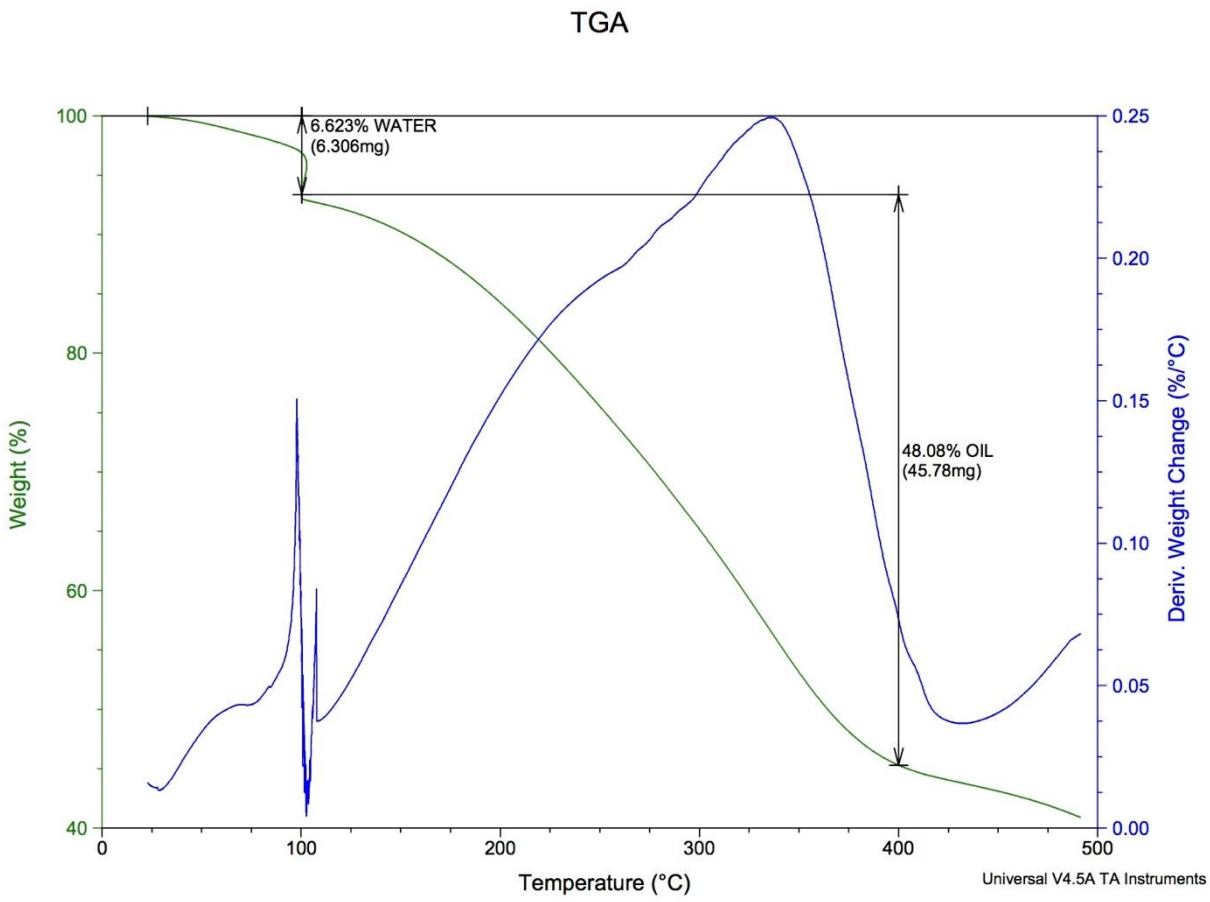


Figure 5-6 TGA of 1.25 ml oil AC

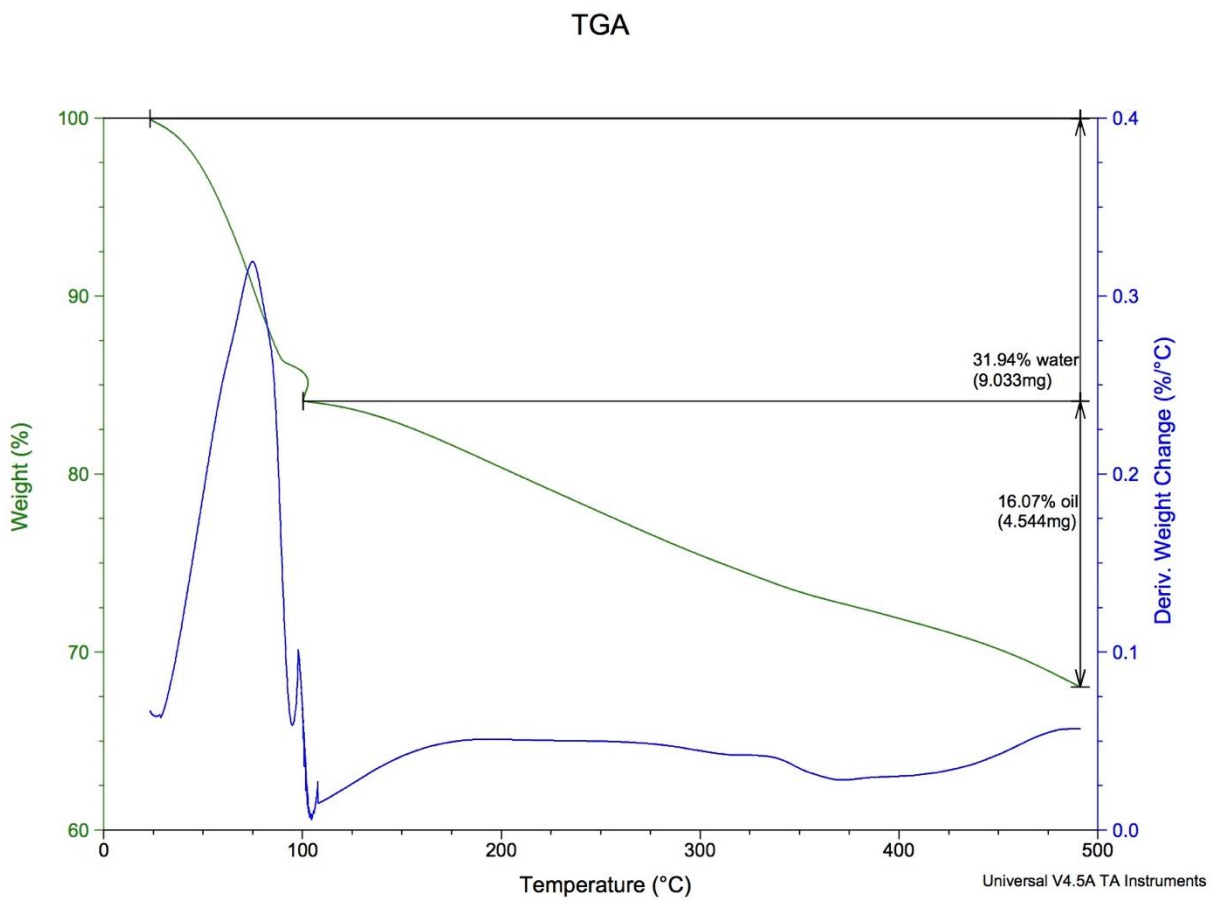


Figure 5-7 TGA of 0.25 ml oil with FA

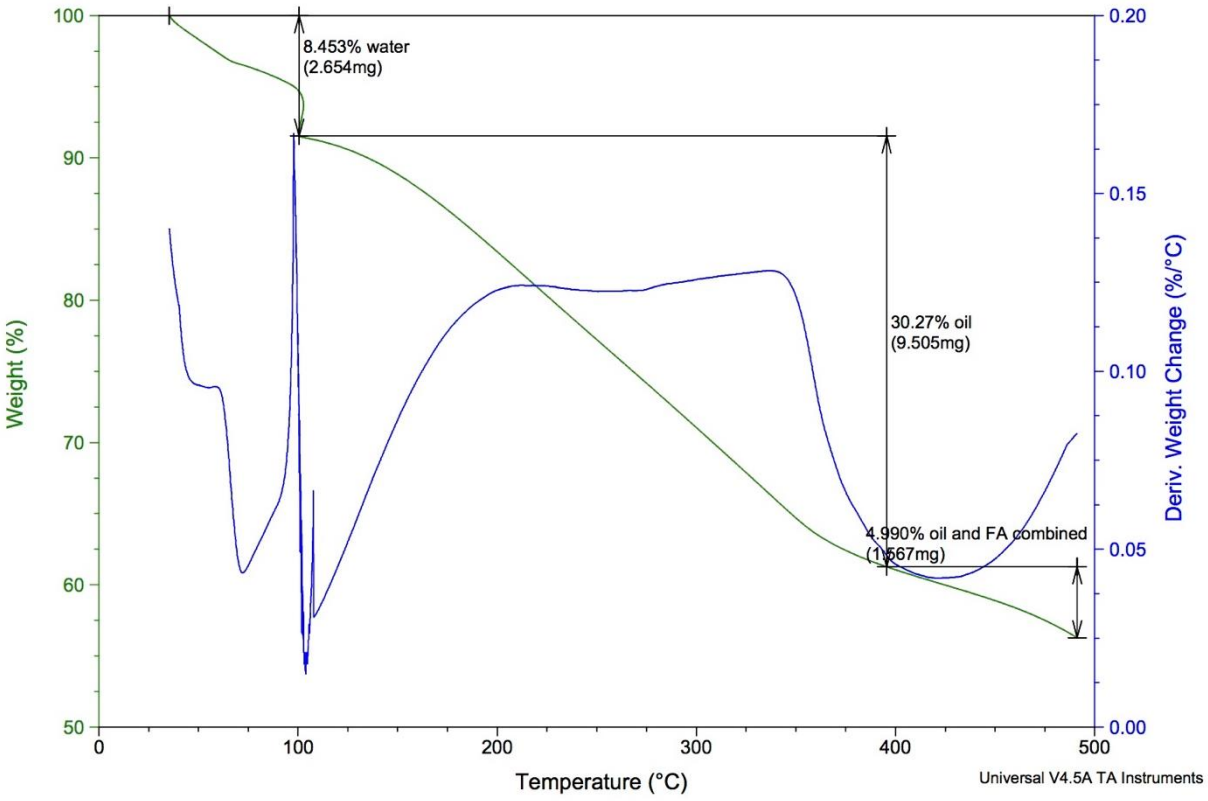


Figure 5-8 TGA of 0.5 ml oil with FA

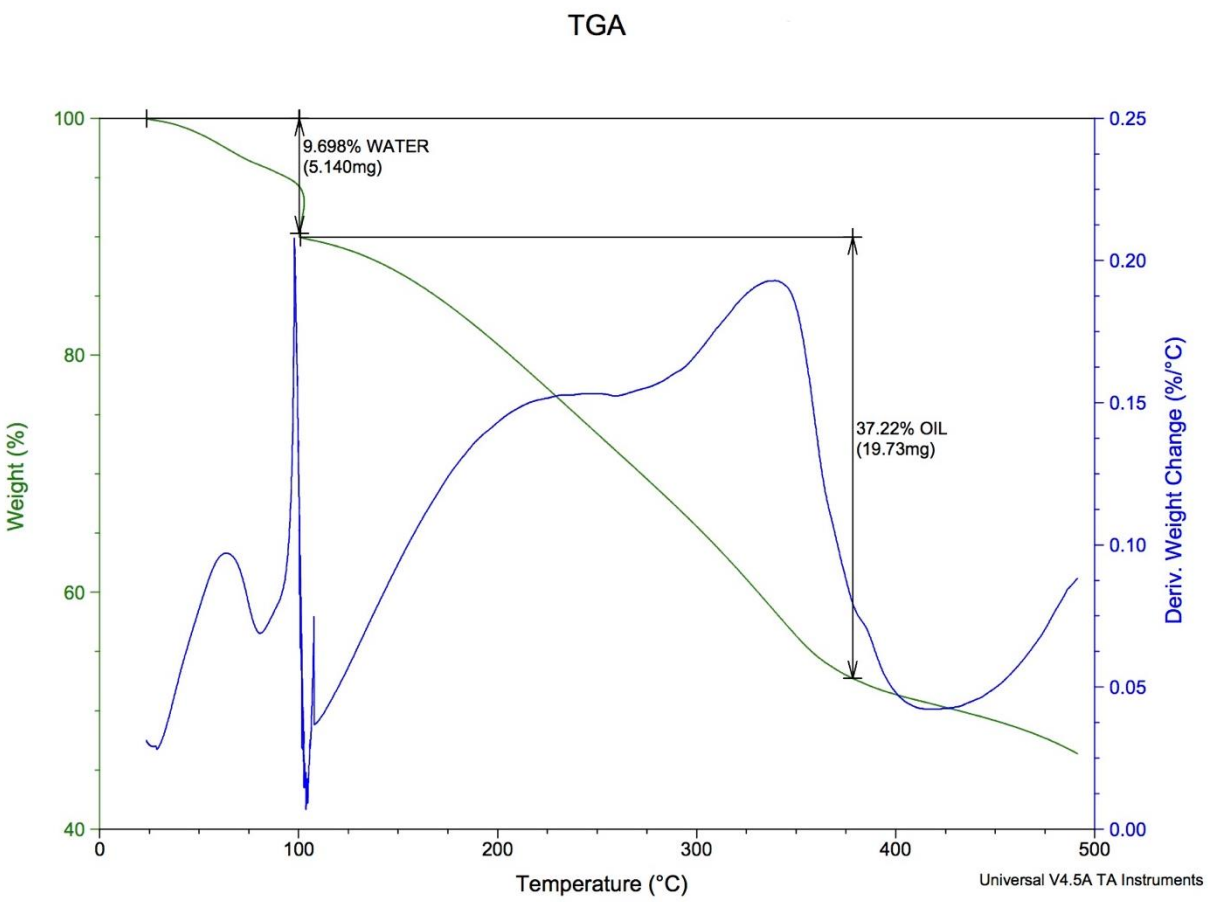


Figure 5-9 TGA of 0.75 ml oil with FA

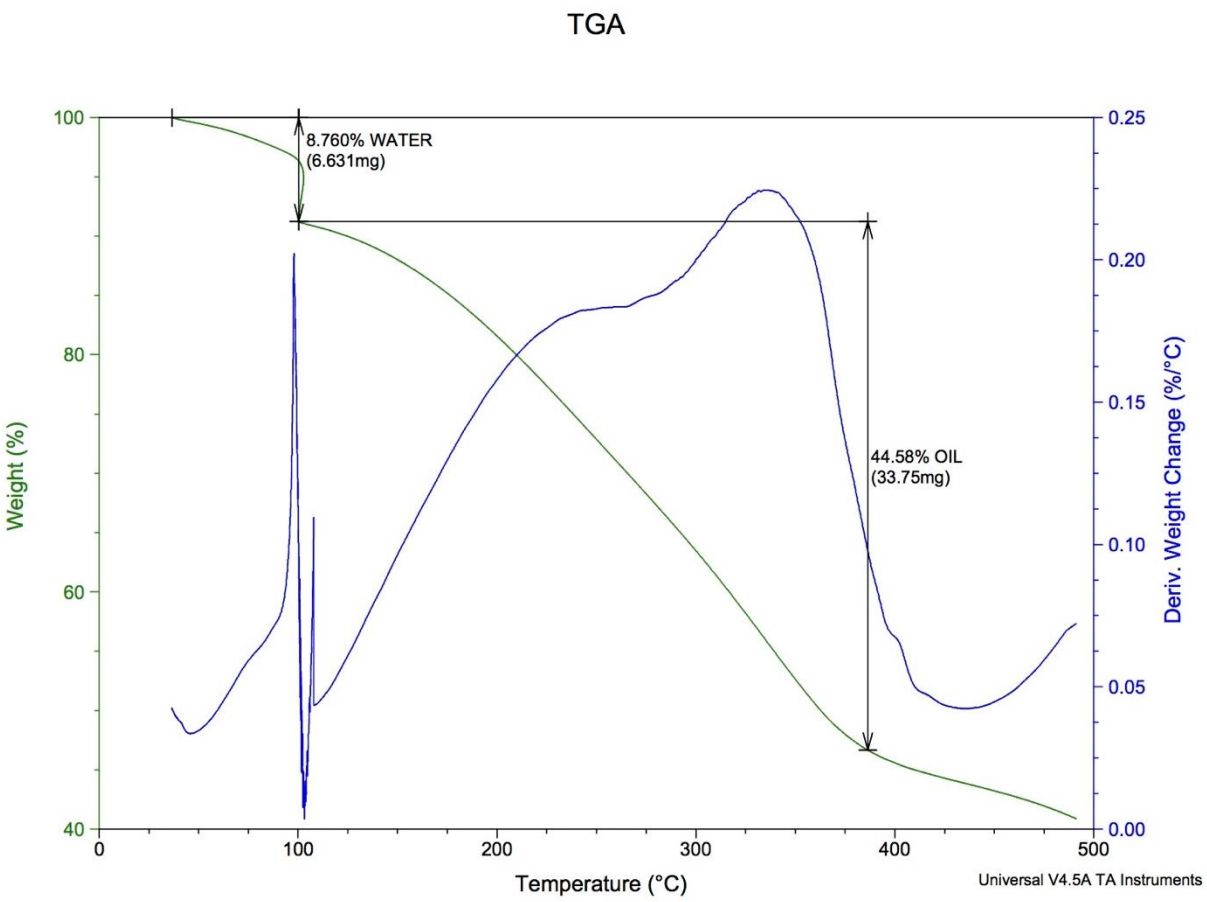


Figure 5-10 TGA of 1 ml oil with FA

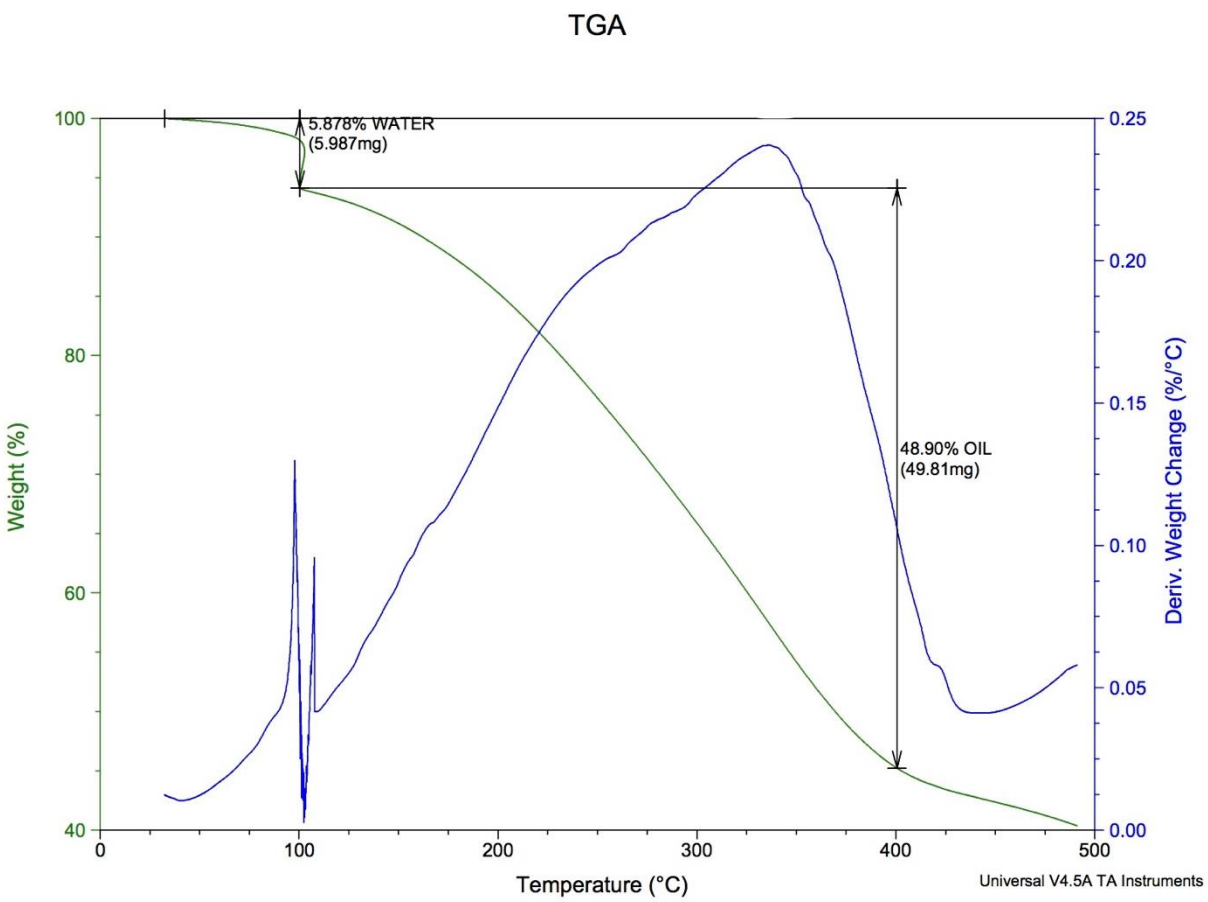


Figure 5-11 TGA of 1.25 ml oil with FA

Table 5-1 AC-OFA and OFA oil adsorption capability

Micro liter of oil per 100 ml seawater	AC-OFA (g/g)	OFA (g/g)
250	0.2296	0.3090
500	0.4658	0.4939
750	0.5667	0.7011
1000	0.8257	0.9554
1250	1.0614	1.0813

Chapter 6. Fly Ash as Composting and Sludge Stabilization

6.1 Background

In order to sanitize and stabilize biosolids and to minimize their detrimental health effects, composting is currently being practiced globally (Tandy et al., 2009). Based on previous research, sludge-based compost can improve soil properties physically by enhancing the soil's ability to hold water, keeping soil particles together, and improving soil porosity. It can also help to return organic matter to the biological cycle. Once artificial fertilizer is replaced by sludge-based compost, significant energy and resources can be saved (Werther and Ogada, 1999, Chen et al., 2012). Although biodegradation occurs during composting, traditional composting is usually not effective in immobilizing heavy metals and organic contaminants. Other emerging contaminants of concern include chlorinated organic compounds, paraffins, plasticizer di-(2-ethylhexyl) phthalate, antibiotic-resistant microorganisms, and pharmaceuticals and endocrine-disrupting compounds present in sewage sludge (Smith, 2009).

Most polycyclic aromatic hydrocarbons (PAHs) are highly toxic and have mutagenic and carcinogenic properties; due to their high persistence characteristics, these compounds do not easily biodegrade or decay. Compost quality can be improved by increasing aeration, immobilizing metals and PAHs, and absorbing moisture from biosolids by adding bulking agents such as rice husks, straw, and sawdust during composting (Zorpas and Loizidou, 2008, Yañez et al., 2009). When biosolids are co-composted with AC and biochar, the immobilization of metals and the reduction of organic contaminants and PAHs (Oleszczuk et al., 2012) significantly improve the

compost quality; due to the high cost of AC, however, the composting of biosolids is not economically feasible.

6.2 Fly ash from CBPP

In this study, FA was collected from CBPP's biomass boilers. Mixed fuels utilized in the boiler are fossil fuel (bunker C and waste oil) and hog fuel (by-products from mill operation, such as bark, sawdust and eluted sludge). The year-round generation and landfilling of FA and bottom ash from CBPP are about 10,000 tons respectively (Telegram, 2010). Although metals in the FA were claimed as stable under general conditions, only when the ash encountered acidic liquids (pH < 4) could these metals possibly leach from the ash. Land use and PM are still matters of concern to human health and ecosystems. CBPP FA generally contains fiber-like structures, has a very high surface area, and is highly hydrophilic. The characterization of CBPP FA is presented in section 6.3.3. Due to its high Al and Ca content, the pH of CBPP FA is extremely high. Although the alkalinity of CBPP FA provides the potential as an soil amendment in neutralizing acidic soils, its high pH of 10 to 12 would be corrosive to soil and plants. Utilizing CBPP FA as the amendment to stabilize municipal sludge was conducted in this study. I investigated the feasibility of composting sewage wastewater treatment sludge with power boiler ash from a pulp and paper plant.

6.3 Characterization of CBPPFA and Biosolids

Characterization of CBPPFA and biosolids contains both physical and chemical analysis, such as pH, moisture, carbon and nitrogen content, metals and PAHs. Physical characteristics can affect the maturity while bioavailability is affected by chemical characteristics. A dewatered and anaerobic treated biosolid and primary sludge sample were collected from the Riverhead Waste

Water Treatment Plant, St. John's, Canada. Dewatered sludge and primary sludge were mixed to ensure the moisture of the compost. CBPPFA were utilized as received.

6.3.1 Moisture content, pH, C/N ratio and metal content

The metal content was analyzed by the method outlined in section 2.1.9. The pH and moisture content were measured by the methods listed in sections 2.1.1 and 2.1.2. Carbon and nitrogen content were measured by the methods listed in section 2.1.6.

6.3.2 Polycyclic aromatic hydrocarbon

PAHs were extracted by solvent extraction technology, followed by GC-MS (Agilent 7890A GC system and 5975C MSD) analysis (Kriipsalu et al., 2008). A 3 ± 0.1 gram compost sample was weighed in a 15 ml conical glass centrifuge tube and 12 ml of extraction solvent (acetone: cyclohexane; v: v= 1: 1) added to it, anhydrous sodium sulfate (Na_2SO_4) can be added to the tube for free of flow purpose, then the tube was placed on a mechanical shaker for 16 hours at 200 rpm. The tube was centrifuged at 3000 rpm for 15 minutes to separate the solvent and the compost. All the solvent was transferred to another 30 ml tube, 6 ml 4% sodium chloride (NaCl) solution added to it, and vortexed for one minute to ensure optimal mixing. The tube was allowed to settle for several minutes to separate the organic phase and the water, and a glass pipette was used to draw all of the organic phase and concentrated by air blowing, 250 µl of hexane was then added to dissolve the extract. The extract was then ready for cleanup, a process using silica gel chromatography: silica gel (SiO_2) and Na_2SO_4 were heated at 450℃ in a muffle furnace for four hours to activate the SiO_2 and to remove volatile matters from Na_2SO_4. Two grams of activated silica gel was weighed in a glass-wool-filled 6-milliliter syringe, then a thin layer of 2 ml of copper

added and an additional 2 ml of Na_2SO_4 on top of the copper powder. After 6 ml hexane conditioning of the column, the sample was added to the column and the first fraction eluted by 6 ml hexane, followed by 6 ml hexane: dichloromethane (DCM) (1:1, v:v) eluting target compounds and 2 ml DCM for medium to high polarity compounds. The hexane and DCM fraction was then air-concentrated to 2 ml for GC-MS analysis.

6.3.3 Characterization result and discussion

The results of the characterization of CBPP FA and RHWWTS sludge are listed in

Table *6-1*. CBPP FA shows very strong alkalinity, pH 12. The pH of RHWWT sludge is 8.7, which is suitable for use as a soil amendment. The high moisture content of the sludge sample could negatively affect the compost procedure; the low moisture content of the CBPP FA can balance the total moisture content to keep it at 55%. The high concentration of Cl in the sludge could be due to the use of detergent and bleach. The Cl content of FA could due to the hog fuel contains effluent sludge. Originally, there is no PAHs found in both samples, crude oil was added as the source of PAHs and to analyze the biodegradation of the composting. Ten percent of all samples were duplicated for quality control.

Table 6-1 Characterization of CBPP FA and RHWWTS sludge

CBPP FA		RHWWT Sludge
pH	12	8.7
PAHs	Not detected	Not detected
Moisture content	0.89%	73%
Metal content in solid (Unit: mg/kg)		
Mg	511.65	6493
Al	947.025	20294
Fe	784.202	18000
P	114.332	7546
S	303.011	Not detected
Cl	11634	22960
Zn	11.724	933.278
Cu	7.280	674.172
Pb	2.252	88.295
As	Not detected	2.947
V	15.460	39.108
Cr	4.725	44.158
Ni	15.962	23.862
Ca	3211.206	10234

6.4 Experiment Design

Two parallel experiments were conducted in two same aerobic compost reactors under the same conditions; however, the CBPP FA was added to only one reactor. The results of these two reactors can be compared to determine the capability of CBPP FA as a stabilizer. Seven kilograms of digested wastewater sludge and 2 kilograms of fish waste processed in a food processer were added to both reactors. An additional 500 grams of the CBPP FA was added to one reactor. The samples were turned twice a day to maintain air flow. Approximately 30 grams of samples were taken on days 1, 3, 6, 7, 9, 12, 15, 18, 21, 24, 27, and 30.

6.5 Result and Discussion

The stability and maturity of a compost are generally determined by the C/N ratio and the GI. In addition to these two parameters, the pH and moisture or water content of a final compost product were also tested. Compost samples were taken every three days over a 30-day period to determine the C/N ratio, GI, moisture content, and pH. Overall 10% of samples are duplicated to ensure the deviation of duplicate results are within 10%. Duplicate results are reported in average and all results are shown in

Table *6-2*.

Table 6-2 Result of composting parameters

Time (days)	Moisture content (%) - W	Moisture content (%) - W/O	GI (%) - W	GI (%) - W/O	pH - W	pH - W/O	EC - W	EC - W/O	C/N ratio - W/O	C/N ratio - W
1	68.45	71.30	21.35	21.37	7.52	7.24	10.16	10.03	10.70	14.02
3	69.95	71.10	23.45	28.01	7.66	7.54	10.09	9.48	10.63	14.78
6	68.98	70.48	21.14	26.00	8.20	7.95	9.8	8.98	10.55	14.56
9	68.79	69.39	24.30	23.20	8.16	8.02	9.505	8.47	10.48	14.27
12	69.80	71.58	28.89	25.07	8.29	8.13	8.5	8.25	10.26	14.18
15	70.57	72.15	26.59	27.26	8.50	8.22	8.16	8.41	10.17	14.12
18	70.20	70.85	29.22	30.79	8.47	7.96	8.29	8.57	10.20	13.95
21	70.19	69.92	31.42	32.92	8.79	7.84	9.905	8.62	10.07	13.74
24	72.37	72.75	28.08	32.94	8.82	8.01	9.18	8.71	9.67	13.85
27	71.65	71.56	33.20	35.33	8.45	7.84	9.28	8.14	9.57	13.64
30	70.54	70.59	29.26	38.22	8.68	8.12	8.84	7.86	9.76	13.72

Where

-W: composting added FA;

-W/O: composting without adding FA

6.5.1 Temperature

Temperature is one of the important indexes of the degree of composting maturity. It is one of the indicators of the removal of most pathogens. Generally, an ideal temperature control of a mesophilic composting system ranges from 45°C to 60°C (Hackett et al., 1999). Figure 6-1 shows the effect of temperature. In this study, the temperature of the sample with FA show graduaal increase to 35°C during the first 15 days, then graduaal decrease to 28°C. The increase of temperature could be contributed to the microorganism growth, and this also matches with the sharp increase of bacterial colony in section 6.5.7. Antizar-Ladislao et al., illustrated that lower temperature can have better performance in the PAHs removal efficiency, about 90% removal at 38°C and 64% at 70°C, respectively (Antizar-Ladislao et al., 2005). Because PAHs are the target contaminants of this study, the relatively lower temperature could be better than the regular optimum temperature.

6.5.2 C/N ratio

Carbon and nitrogen are important nutrients; microbes use carbon for energy and growth, and nitrogen for protein and reproduction. Biosolids mixed with FA in a ratio of 14:1 were composted for 30 days, and the biosolids only was treated under the same conditions for comparison. Figure 6-2 shows the C/N ratio change with two types of compost, biosolids and biosolids with FA, over a 30-day composting process and that the addition of FA can significantly increase this ratio because the existence of amorphous carbon in FA. However, the C/N ratio change for the two types of compost for this time period has similar trends and slope, which indicates that FA may not accelerate composting. The C/N ratio of biosolids with FA decreased from 14.0 to 13.7; that

of biosolids dropped from 10.7 to 9.8. Both types of compost have a slight C/N ratio change, indicating that composting is quite slow in both systems.

6.5.3 Germination index (GI)

GI is commonly used for evaluating compost maturity, especially when compost products are applied to soil supplements or used as fertilizers.

Figure 6-3 displays seeds sprouting in biosolids with FA and in sole biosolids. Within a 30-day period, the highest GI in biosolids with FA is 33.2%; and in the biosolids is 38.2%. A compost with a GI value of more than 80% indicates a phytotoxic-free and mature compost (Zucconi et al., 1981). This result reveals that both types of compost are not mature enough, and an extended composting time is necessary. Compared with biosolids without FA, the addition of FA hinders seed germination. Therefore, a further study is necessary to investigate phytotoxic compounds in FA.

6.5.4 Moisture content

Moisture is essential for microbe growth: the ideal level is 40%-60%. Figure 6-4 shows the change of moisture in two types of compost during the composting process. A fluctuation of moisture is observed in both materials. The moisture content of biosolids with and without FA fluctuates between 68.5% and 72.4%, and 69.4% and 72.7%, respectively. This illustrates that both have a moisture content slightly higher than 60%, which could be why the degradation process is retarded.

6.5.5 pH

The pH indicates the alkalinity or acidity of the compost. During the microbial decomposition of organic compounds, ammonium (NH^{4+}) is usually generated, leading to a pH increase to above 8. As biodegradation continues, NH^{4+} is emitted from the medium as NH_3; meanwhile, some produced organic acid neutralizes the compost, which further decreases the pH. The pH of the compost will stabilize (Wichuk and McCartney, 2010). Figure 6-5 demonstrates the change of pH in two types of compost over 30 days. The pH of both biosolids with FA and sole biosolids gradually increases to above 8 at the end of the 30-day period. This implies that both materials are possibly in the process of NH_3 generation, and not yet mature. This is in good agreement with the results of other parameters.

6.5.6 Electrical conductivity (EC)

EC, determined at different sampling points to estimate the salinity and soluble nutrients in the compost, indicates whether the compost can be applied as a growth medium or an organic fertilizer. High levels of salt in compost can reduce crop yields as it hinders the root from extracting water from the soil-compost solution. In general, most crops can grow in a compost with an EC below 10 mmhos/cm. Once the EC is above 10, the compost is better utilized as an organic fertilizer (Hackett et al., 1999). As shown in Figure 6-6**Error! Reference source not found.**, the EC values of the two types of compost fluctuate between 7.9 and 10.2 mmhos/cm, which denote that both can potentially be applied as a growth medium. Both samples show the reducing trend of EC, which is due to the leaching of salts.

6.5.7 Microorganism counting

Microorganism colonies were counted by the spread plate counting method. The culture medium for total thermophilic and mesophilic bacteria was 10% strength tryptic soy broth agar. A 10 gram sample was weighed in a 250 ml Erlenmeyer flask with the addition of 90 ml of a 0.85% (w/w) sterile NaCl solution. The flask was sealed and mixed on a mechanical shaker at 200 rpm for 30 minutes at room temperature. The supernatant was diluted into ten serial concentrations ranging from 10^{-2} to 10^{-10}. Four dilution factors were selected that could best characterize the microorganisms of the samples. Then 100 μL diluted solution was spread in a petri dish with the medium, and placed in a 30°C incubator for three days. The results are shown in Figure 6-7. The microorganism of the sample with FA begins with higher level, then slightly decreases in the first three days, reaches a peak at the sixth day, begins to decrease, and reaches another peak at the 21st day. This could be due to the unstable conditions of composting in the first week, and with the increase of temperature and aeration, thermophilic bacteria begin growing, then decrease after the peak. The sample without FA shows a more stable trend than that with FA; this could be because, without FA, there is insufficient carbon for bacteria growth, thus causing the slower maturity of the composting process. After 21 days composting, the PAH concentration was stable from both samples. This is considered the saturation of microorganism.

6.5.8 PAH degradation

Free PAHs in the compost system is one indicator of biodegradation for persist organic contaminates. As shown in Figure 6-8, the concentrations of extractable naphthalene (NAP) and Phenanthrene (PHEN) from both compost samples decrease during composting procedure. The

one with FA shows a better performance of NAP reduction than the one without FA; this could be contributed to the addition of high surface area FA. The high surface area and rich of micro porous structure can eventually improve PAH adsorption. Oleszczuk (2012) illustrated that AC enhanced composting can effectively degrade five to six rings' PAHs from pore water of contaminated soil; however, for two to four rings' PAHs, AC is barely effective (Oleszczuk et al., 2012). In this study, 2-3 ring PAHs were well controlled by FA aided composting. As Antizar-Ladislao et al., (2005) reported that the optimum biodegradation temperature of PAHs is 38°C, while the temperature in this study for both processes ranged from 26°C to 38°C, this can greatly help biodegradation of PAHs (Antizar-Ladislao et al., 2005). Small molecular weight PAHs can be adsorbed by FA or evaporated by aeration.

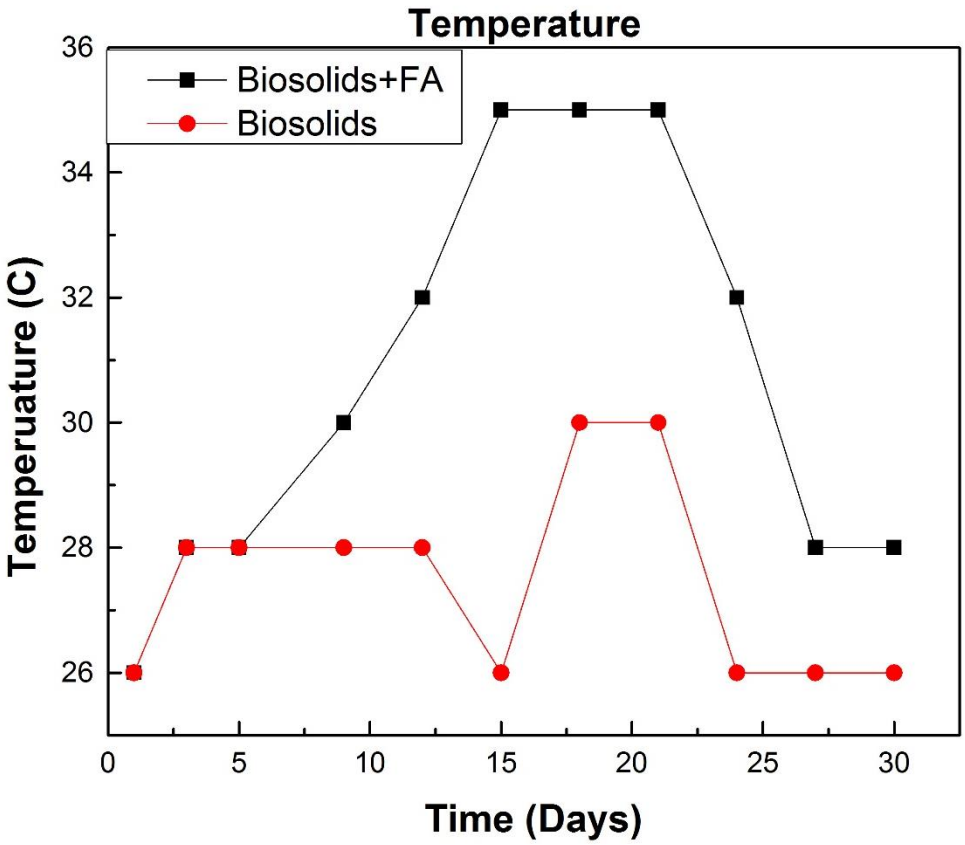


Figure 6-1 Temperature of compost with and without FA

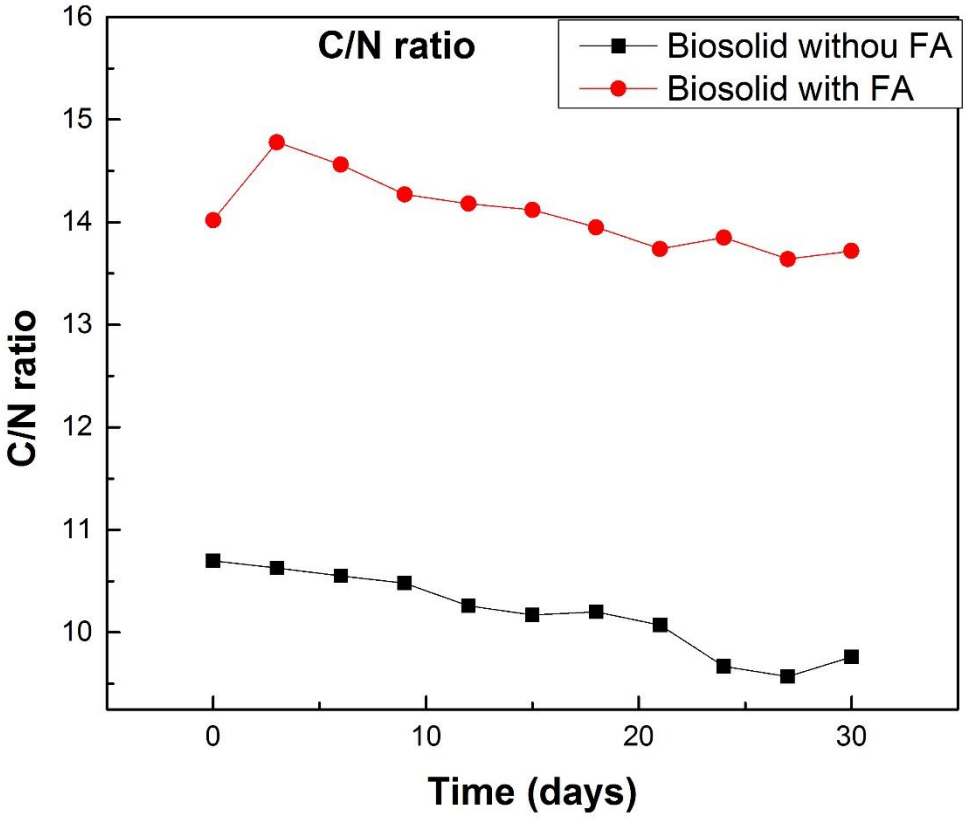


Figure 6-2 C/N ratio of compost with and without FA

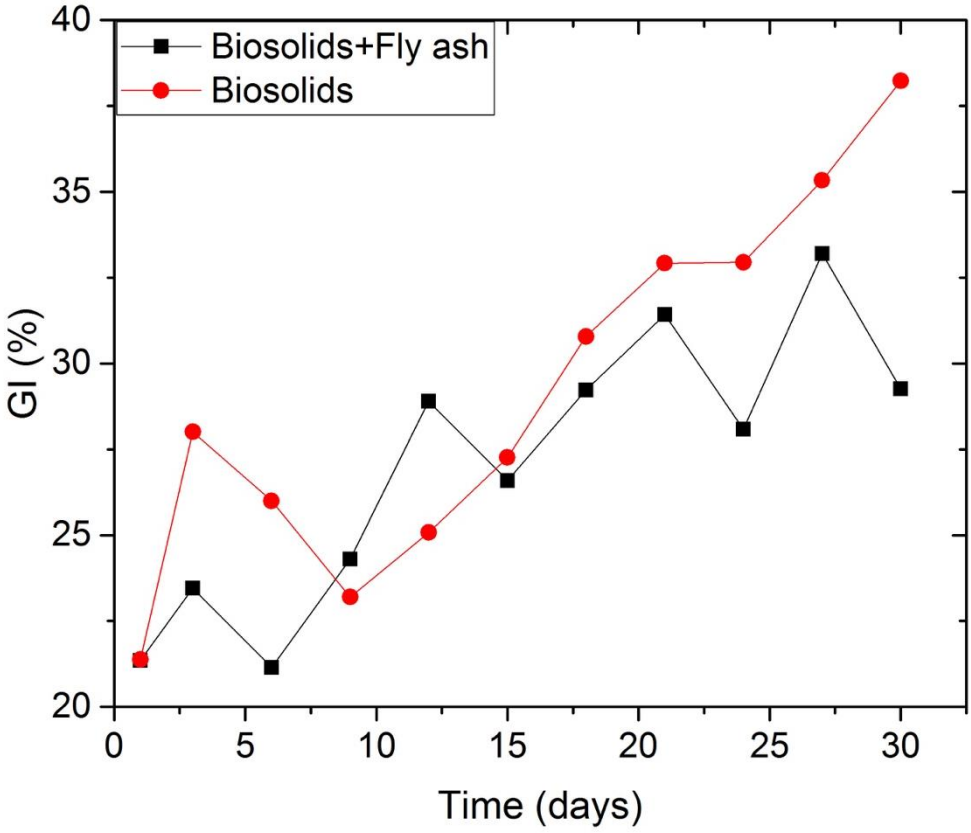


Figure 6-3 GI of compost with and without FA

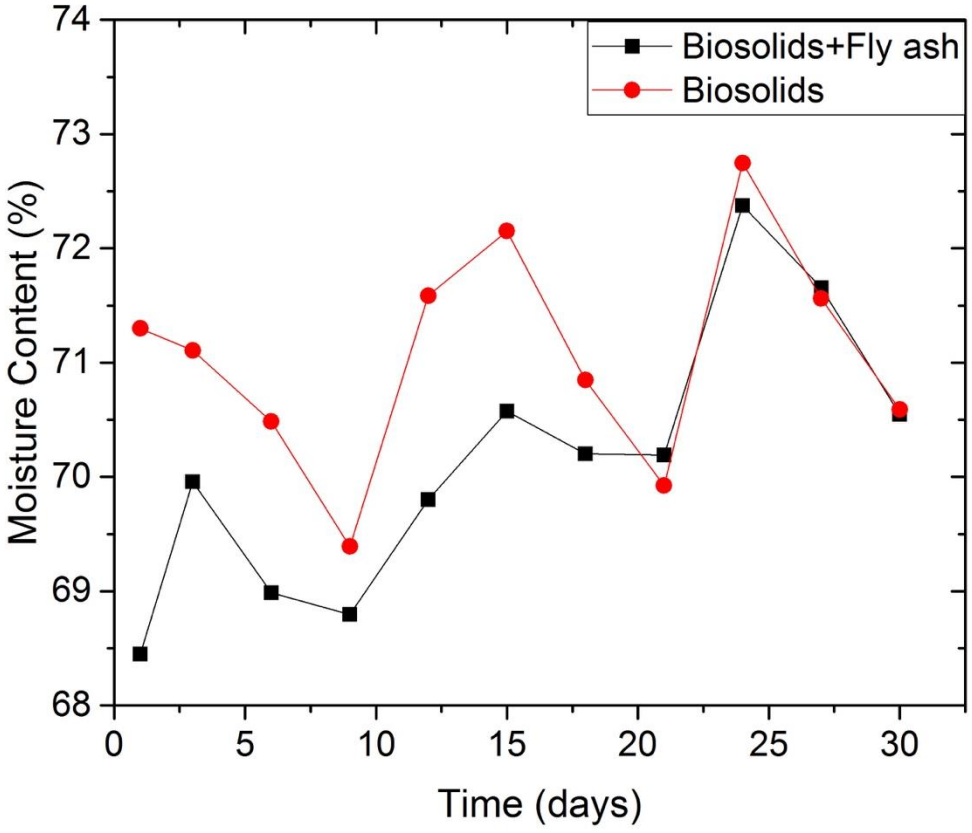


Figure 6-4 Moisture content of compost with and without FA

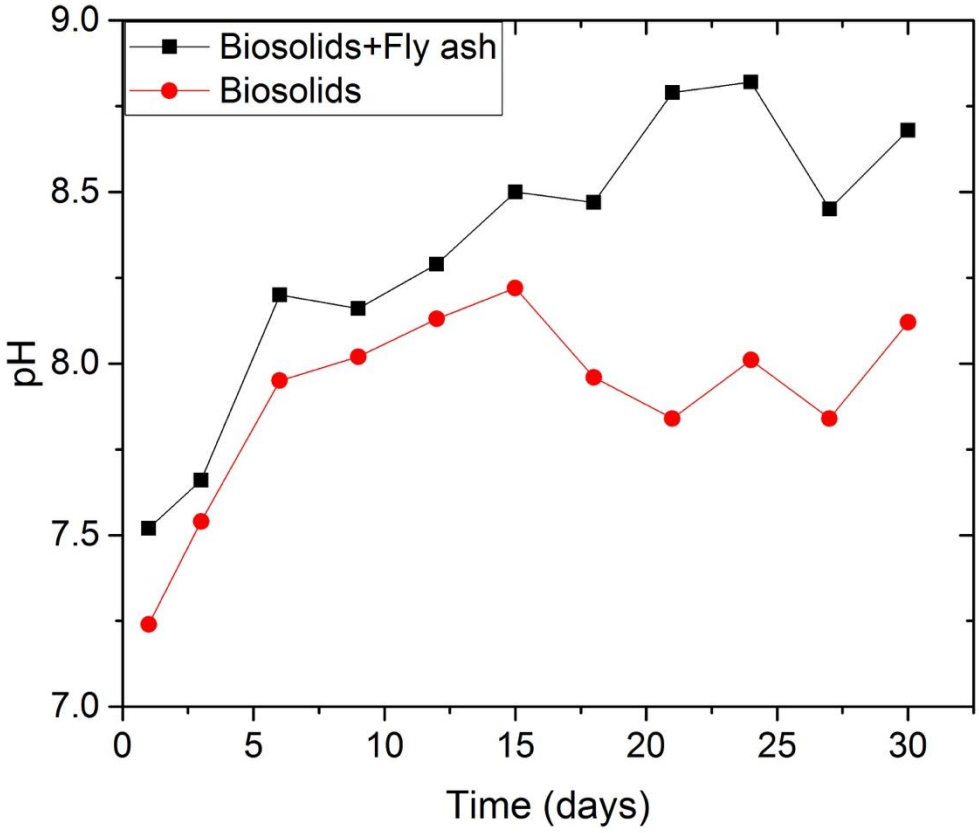


Figure 6-5 pH of compost with and without FA

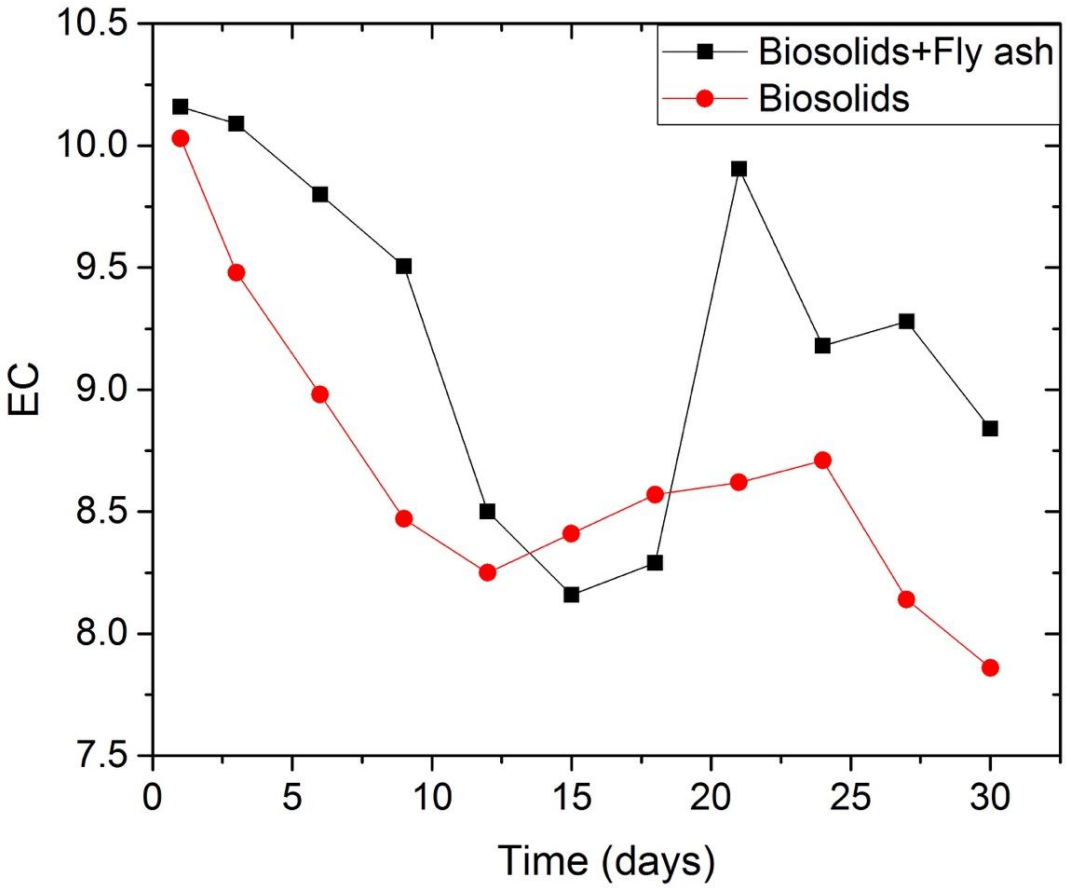


Figure 6-6 EC of compost with and without FA

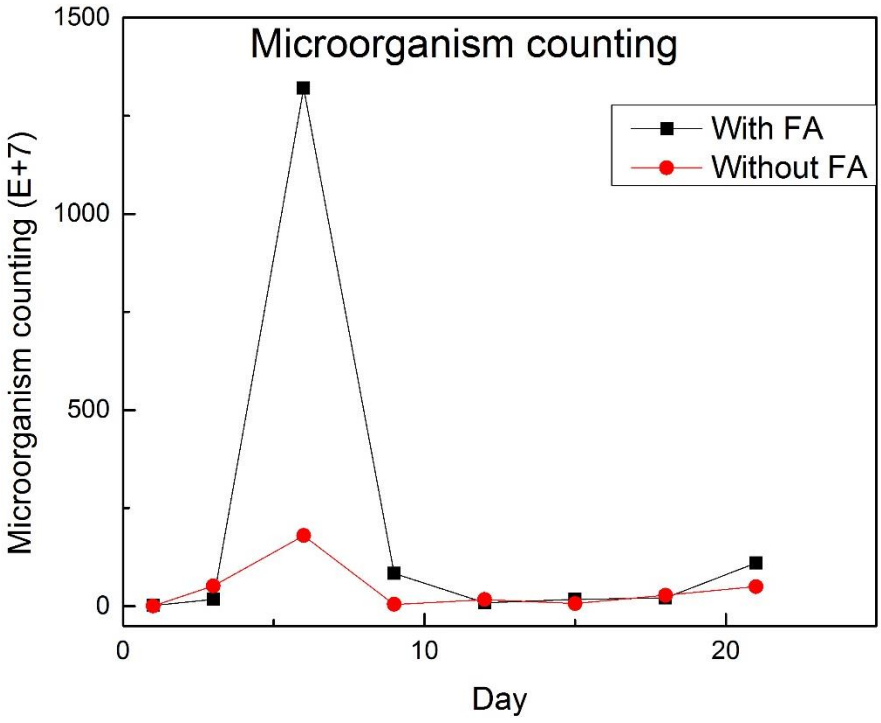


Figure 6-7 Microorganism counting of compost with and without FA

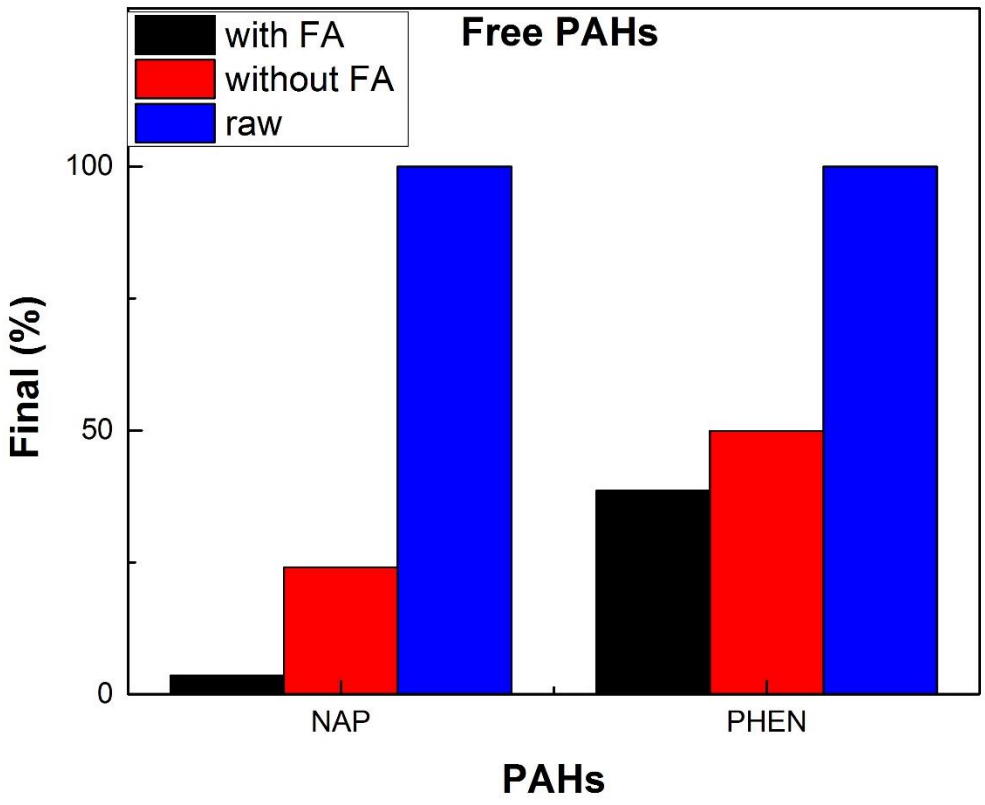


Figure 6-8 Free PAHs of compost with and without FA

Where:

Final (%): the relative PAH concentration calculated by $\frac{C_{30}}{C_i}$

C30: concentration of PAH at 30 days

Ci: initial concentration of PAH

Chapter 7. Conclusions and Recommendations

7.1 Summary

In this research, two types of FA samples (OFA from oil-fired power plant and a CBPP FA from pulp and paper plant) were investigated. OFA was collected from Saudi Arabia, and the CBPP FA was collected from the CBPP.

Chemical and physical characterization were conducted to provide the comprehensive study of two different FAs. Since these FAs are being generated from different raw materials, their characteristics vary considerably. CBPP FA shows a high surface area and microporous structures, while OFA has a very low surface area and a non-porous structure. Response surface method was applied to study the adsorption of TOC by OFA. The study shows that the carbon dosage and pH can significantly affect the TOC removal rate. Adding as much carbon and adjust pH to acid condition can greatly help TOC removal. OFA was also utilized in the batch test to simulate off-shore oil spill cleanup. The study shows that the surface area can be a key factor of oil absorption. Carbon extracted from FA and without activation shows a good potential in oil absorption. Oil absorption weight by unit carbon can be up to 1 g/g and more. The weight of absorbed oil from the oil/water system is linear to the weight of oil added. The composition of both FAs also indicates that OFA has the potential for valuable metals extraction, such as V and Ni while the high carbon content and high pH of CBPP FA has the potential to be the carbon source in the composting system, however; utilizing FA and sludge alone could decrease the quality of compost and bioavailable nutrients for the bacterial growth are required. The parallel compost procedures were

performed to examine the ability of PAH degradation. The result indicates that the mixture of sludge and CBPPFA can eventually degrade PAH.

7.2 Major research contributions

This research is focused on economically and environment friendly extraction and reuse of carbon from FA, Major contributions made from this research are listed below;

1. Developed optimum condition to extract clean carbon from OFA by minimizing acid use and energy consumption;
2. Developed optimum condition for TOC removal to minimize formation of DBPs in the rural communities in Newfoundland with potential to develop an affordable water treatment system in small communities;
3. The study shows outstanding performance to aggregate and adsorb crude oil, which could potentially use to control emergency oil spill and spreading effectively and economically;
4. CBPPFA aided composting showed significant reduction in PAHs.

7.3 Recommendations and future work

The following recommendations are made from this study:

1. The AC from OFA should be tested following the standard protocol of leaching tests to ensure that it meets the standards for water treatment.
2. The carbon in raw OFA shows prominent level of graphitic carbon. It is therefore recommended to conduct a study on the separation of graphite to single layer graphene.
3. AC from OFA has a good potential to be used as an affordable adsorbent for the removal of organic matter from water but it has low surface area and pore volumes. It is therefore

proposed to conduct an in-depth investigation on the improvement of surface area and development of pore volume to make it competitive with the commercial AC.

4. Surface modification of OFA should be studied to make it more hydrophobic for off-shore oil spill cleanup.
5. To increase oil absorption capacity, the OFA should be modified to develop sponge/aerogel type of materials.
6. AC-FA utilized as a composting additive needs more in-depth studies to improve C/N ratio.

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